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A Comparison of Physical and Electrochemical Properties of Two Ionic Liquids Containing Different Cations: 1-Butyl-1-Methyl-Pyrrolidinium Beti and 1-Butyl-3-Methyl-Imidazolium Beti

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A COMPARISON OF PHYSICAL AND ELECTROCHEMICAL PROPERTIES OF TWO IONIC LIQUIDS CONTAINING DIFFERENT CATIONS: 1-BUTYL-1-METHYL-PYRROLIDINIUM BETI AND 1-BUTYL-3-METHYL-IMIDAZOLIUM BETI

A thesis submitted in partial fulfillment
of the requirements for the degree
of Master of Science

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Edward Nelson Kennedy Entitled A Comparison Of Physical And Electrochemical Properties Of Two Ionic Liquids Containing Different Cations: 1-Butyl-1-Methyl-Pyrrolidinium Beti And 1-Butyl-3-Methyl-Imidazolium Beti BE ACCEPTED IN PARTIAL FULFILLMENT FOR THE REQUIREMENTS FOR THE DEGREE Master of Science.

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ABSTRACT

Kennedy, Edward Nelson M.S., Department of Chemistry, Wright State University, 2009. A Comparison Of Physical And Electrochemical Properties Of Two Ionic Liquids Containing Different Cations: 1-Butyl-1-Methyl-Pyrrolidinium Beti and 1-Butyl-3-Methyl-Imidazolium Beti.

A novel ionic liquid, 1,1-butyl-methyl-pyrollidinium bis-pentafluoroehthanesulfonylamide (BMPyrrBeti) was synthesized and characterized . Its physical and electrochemical properties compared to a similar ionic liquid containing the imidazolium cation, 1-methyl-3-butyl-imidizolium bis-pentafluoroehthanesulfonylamide (BMImBeti). The two ionic liquids contain the same anion, bis((pentafluoroethane)sulfonyl)imide (Beti), and the same two alkly group substituents (a methyl and a butyl group). The two ionic liquids differ only by the cation component, and the connectivity of the two substituents (1,1 for the former, and 1,3 for the latter).

The following physical properties of BMPyrrBeti were measured and compared to the same properties of BMImBeti: conductivity, viscosity, absorption and desorption of water, and thermal properties (TGA and DSC). The electrochemical properties of BMPyrrBeti were also measured.

It was found that BMPyBeti was less conductive than BMImBeti, however this was mostly at higher temperatures. Viscosity measurements revealed that BMPyrrBeti was more viscous as BMImBeti, which often correlates inversely with conductivity, as in this case. Thermal decomposition by TGA occurred at an average temperature of 432 ºC verses 410 ºC for BMImBeti, or 105% percent higher. The freezing point of BMImBeti could not be determined by DSC. The freezing point of BMPyBeti was -38 ºC. The electrochemical window of the new ionic liquid BMPyBeti was very wide, reaching a

maximum of 6.5V. This was 144% percent wider than BMImBeti (4.5V). The diffusion coefficient of BMPyrrBeti was determined to at 25.4 °C and 50 °C from cyclic voltammetry of Ferrocene in NBu_4PF_6.

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DEDICATION

I would like to dedicate my thesis to my Grandmother. She enabled me to go to college and find my way there. I thank her for all she was to her family and me. She is never far from my thoughts. It was my privilege to be her grandson.

I would also like to thank my mother. She has always been supportive of me and believed in me. I hope to be able to repay her.

I would also like to thank my wife. She has never complained about my return to school, even though it meant a substantial drop in income. She was been wonderful through my journey towards my degree.

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I would like to thank Dr. Katovic for his mentorship and his guidance. I would also like to thank him for being someone with whom I genuinely enjoy being with.

I would also like to thank my fellow graduate students, Charlie, Chuck, Jodie, and Jen for being great people to talk chemistry with.

Finally, I would like to thank Dr. Lunsford and Dr. Bombick for helping me to successfully defend this work.

I. INTRODUCTION

Ionic Liquids

Ionic liquids (ILs) are class of compounds composed entirely of ions with melting points below 100 °C. Normally, ionic liquids consist of a nitrogen-containing organic cation such as N,N',N",N''' - ammonium, N,N'-dialkylimidazolium, N,N-dialkylpyrrolidinium or N-alkylpyridinium.[1]

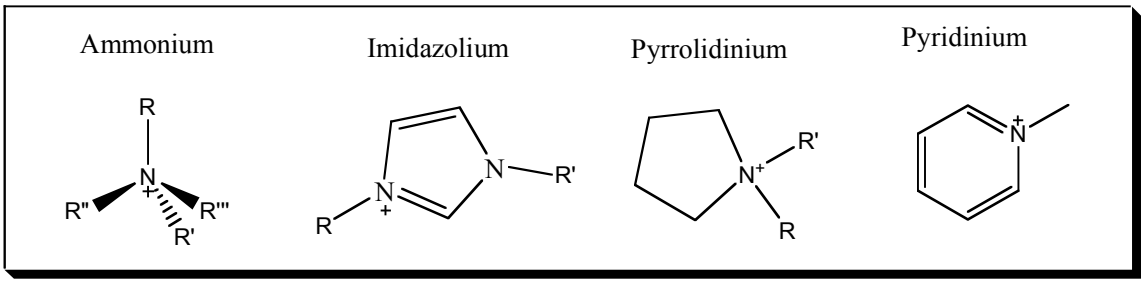

Figure 1. Commonly used cations for ionic liquids.

The anion may be either organic or inorganic and the most commonly used ionic liquid anions include tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), and bis[(trifluoromethyl)sulfonyl]imide anion $(CF_3SO_2)_2N^-$ (also known as bistriflylimide (Tf_2N^-), and the bis-pentafluoroehthanesulfonylamide, or Beti anion, shown in Figure 2.

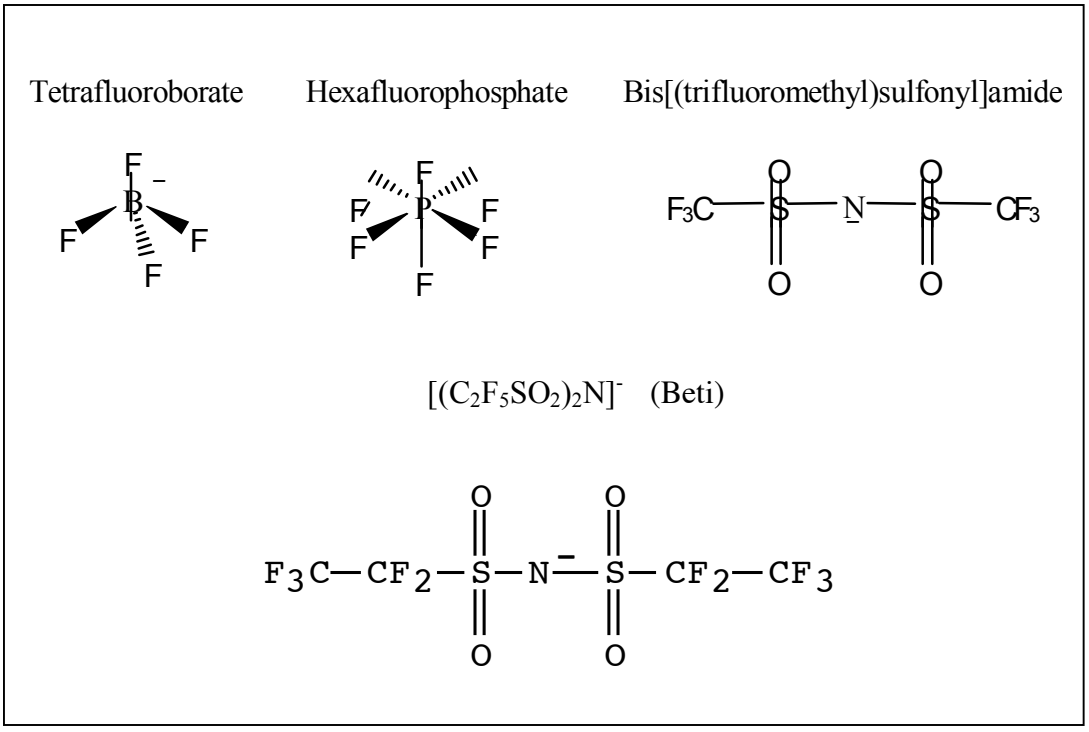

Figure 2. Commonly used anions for ionic liquids.

Ionic liquids have many advantages and potential uses. They are greener replacements of traditional volatile organic solvents (VOS), or conventional organic solvents (COS). They exhibit high ionic conductivity (which make them useful as electrolytes), a low melting temperature, have no measurable vapor pressure, are stable in air, and possess a large liquid state range. They are non-explosive, non-oxidizing, cheap and easy to synthesize and can solvate a wide range of species, including organic, inorganic, and organometallic compounds.[3]

History of ionic liquids

The roots of ionic liquids go back over one hundred years and are firmly planted in traditional high-temperature molten salts.[4] The quest for useful molten salts with lower

melting temperatures led to the discovery of inorganic chloroaluminates, organic chloroaluminates, then to the water and air stable salts now being developed for green chemistry applications.

The motivation for using molten salts in the first place (when water and other molecular solvents are more convenient) is the great stability of their salts – thermally, chemically, and electrochemically.[4] They concurrently possess the qualities of non-volatility and thermal stability, which confers upon them a very wide liquidus range.[4] Furthermore, because they are typically derived from minerals that are naturally occurring, they are inexpensive and available in large quantities. Finally, due to their very high electrical conductivity (from the high concentration of ions) and wide electrochemical windows, they are premier solvents for many electrochemical processes.[4]

Molten salts also have a downside – very high melting points (800 ºC for NaCl, and the relatively "low"- melting mixture, LiCl-KCl, which melts at a balmy 355 ºC). Thus, the applications of these molten salts are limited; appreciable energy costs are needed to maintain these high temperatures, and there are serious compatibility problems with other materials. What was needed was a new type of liquid (or *neoteric* liquid) that retained the strengths of molten salts, without the liabilities. Ionic liquids represent this liquid, or, non-aqueous solvent.

The transition stage between molten salts (like LiCl-KCl) and the current ionic liquids (which contain quaternary cations such as pyrrolidine or imidazole) were the inorganic chloroaluminates. The impetus for examining inorganic chloroaluminates involved a problem the Air Force was having with thermal batteries, which had been operating with molten salts as their electrolytes. Not surprisingly, the problems were temperature-related, and there was a need to develop electrolytes with far lower melting

points. The alkali chloride-aluminum chloride system was chosen. This system was liquid as low as 175 ºC. However, this is still a difficult temperature to work with in a lab and aluminum chloride acts as a very strong Lewis acid – in *all* phases.

Early in their work on molten salt electrolytes for thermal batteries, the Air Force Academy researchers surveyed the aluminum electroplating literature for electrolyte baths that might be suitable for a battery with an aluminum metal anode and chlorine cathode. They found references to work done at the Rice Institute by Frank Hurley and Thomas Wier on electro-deposition of aluminum in some $AlCl_3$-based molten salts that were liquid at room temperature.[5] The electrolytes were mixtures of $AlCl_3$ and 1-ethylpyridinium halides, mainly the bromide.[6]

A literature search uncovered that mixtures of $AlCl_3$ with 1-ethylpyridinium halides (bromides mostly) were liquid at room temperature. Soon after, 1-butylpyridinium chloride-aluminum chloride mixtures were developed, and this marked the beginning of the modern era. There was still a problem however – the chloroaluminates anion is reactive with water, producing corrosive HCl.

In 1990, Professor Mike Zaworoto (working with John Wilkes) from Halifax took a sabbatical with the goal of preparing a characterizing salts with dialkylimidazolium cations, yet with water-*stable* anions. This introduced a new aspect to this growing field. His new tetrafluoroborate, hexafluorophosphate, nitrate, sulfate, and acetate salts were prepared by metathesis reactions of ethyl-methylimidazolium chloride with a sodium halide and were stable towards hydrolysis (at least at room temperature).[4] It was learned that the use of large anions, anions with many degrees of freedom, large cations, and unsymmetrical cations should all result in lower melting points. Due to their (relatively)

high viscosity, glass states rather than crystal states should ensue upon cooling. This brings us to the current state of ionic liquids.

Distinctions between Molten Salts and Ionic liquids

A suitable definition of ionic liquids that would serve as an historic definition, is that ionic liquids are salts having a melting temperature below the boiling point of water. Ionic liquids have been grouped together with molten salts, and refined only by modifying the term ionic liquid with "room temperature ionic liquid (RTIL)" if the ionic liquid is liquid between 20 - 30°C. However, as Wilkes points out, this difference is literally more than one of degree; the practical differences are enough to justify a separate nook for ionic liquids that are liquid at room temperature. For example, their strong ion-ion interactions are not usually seen in higher-temperature molten salts. In practice, these RTILs can usually be handled like ordinary solvents.

Synonyms for materials that meet the *working* definition of ionic liquid are 'room temperature molten salt,' 'low temperature molten salt,' 'ambient temperature molten salt,' 'ionic fluid' and 'liquid organic salt'.[4] Of course, the term "neoteric solvents" are also used, but this can include any type of new solvent.

Characterization of ionic liquids

Ionic compounds typically exist as solids, due to their extremely high melting points (600ºC – 1000ºC).[7] This is, of course most likely to be the case when the cation-anion pair exists as simply atoms, where they then act as "point charges", and can form lattices due to their coulombic interactions.

Ionic liquids differ in geometrically significant ways. Compared to typical solid ionic compounds, ionic liquids contain larger, more complex (the cation can contain branched side chains also), and less symmetrical molecules. Typically, ionic liquids are comprised of a nitrogen containing organic cation and either an organic or inorganic anion. Usually, the nitrogen is a heteroatom in an organic five or six-membered ring. This ring may be aromatic (as it is in imidazolium cations), or not (as in pyrrolidinium cations). The anion may be organic or inorganic. It may be relatively small, as with BF_4^-, or relatively large, as with the bis((pentafluoroethane)sulfonyl)imide (BETI) group. The charges on these ions can be delocalized to an appreciable extent. Although they are ions, these structural features reduce the ability of these liquids to form a solid phase. In fact, the melting point for some ionic liquids can be quite low (-96°C to 100º C).[7]

In 2005, Mihkel, K. reported that the literature on ionic liquids is growing almost exponentially every year (See Figure 3).[8] Factors accounting for this interest include the ease of preparing salts with differing ionic components. Both the cation and anion can be changed, and an infinite number of possible combinations exist. Changing the cation, the cations' side chains, or the anion, allows for "tunability" of these versatile liquids. This allows for the production of a class of solvents with similar physical properties, yet different chemical properties. They can be made more hydrophobic, for example, by increasing the alkyl chain length on the cation. This confers an advantage to ionic liquids over conventional solvents when used as liquid-liquid extraction processes, such as high efficiencies and high selectivities of separation. With their low volatility and their wider range of operational temperatures and conditions, ionic liquids are good candidates for use as electrolytes in batteries, solvents in electrochromic windows, fuel cells, sensors,

and solvents.[8]

Table 1. Growth trend in publications of ionic liquids by year.[12]

Year	Number of Publications	Year	Number of Publications
1985	20	1996	25
1986	22	1997	37
1987	25	1998	41
1988	17	1999	49
1989	20	2000	126
1990	20	2001	250
1991	22	2002	500
1992	24	2003	745
1993	20	2004	1200
1994	15	2005	1389
1995	21	2006	1980

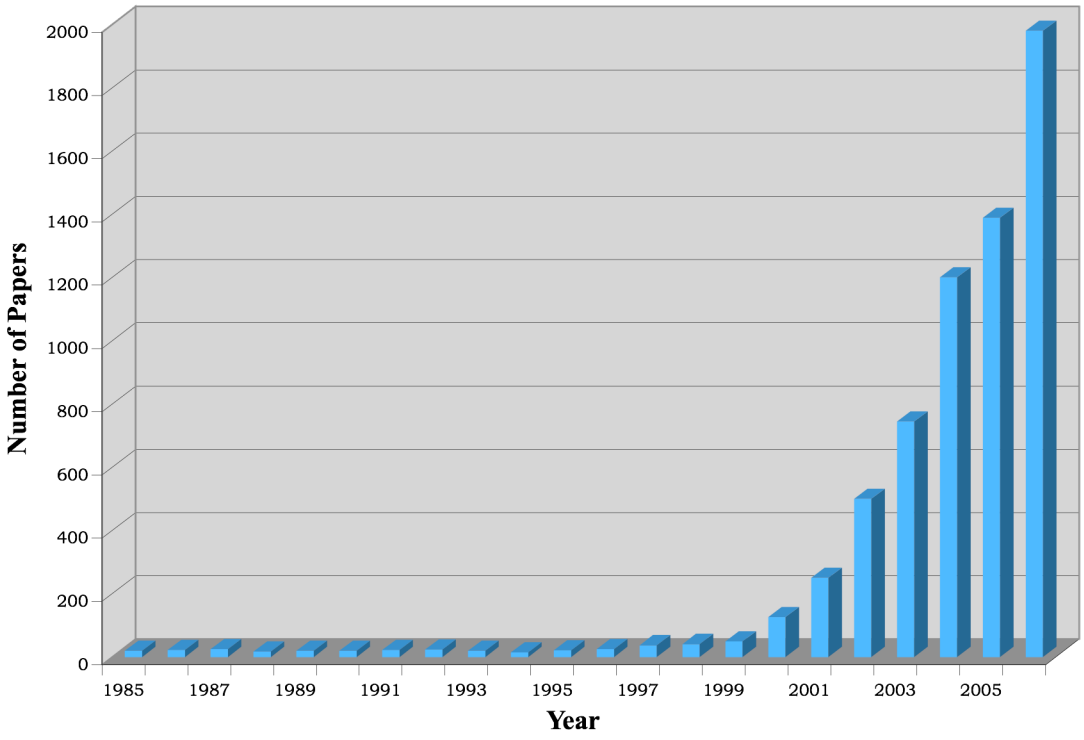

Figure 3 Publications on ionic liquids from 1986 – 2006.[12]

Properties of ionic liquids

The reasons for this rapid growth in interest are not surprising when the properties and uses of ionic liquids are taken into account. They can claim the following physical and chemical attributes:

	Properties	Solvent Uses
Chemical and Physical	-They are greener replacements of traditional volatile organic solvents (VOS), or conventional organic solvents (COS). -High ionic conductivity -Low melting temperature -They have a large liquid state range. -Are viscous liquids -Have no measurable vapor pressure -Are non-explosive, non-oxidizing -Are cheap and easy to synthesize -Able to solvate a wide range of species, including organic, inorganic, and organometallic compounds -Are composed of poorly-coordinating cations -Contain flexibility of structure -Are Stable in air -Are immiscible with a number of organic solvents - Have melting points range between -96°C to +80°C	-They do not evaporate like other solvents -They can be used in chemical synthesis, particularly catalysis -They have the potential to make synthetic processes more efficient -Can be used in separation technology -Are highly polar non-coordinating solvents -Provide a non-aqueous, polar alternative for two-phase systems

	Properties	Solvent Uses
Electrochemical	-High conductivity -Wide electrochemical windows. *The window can differ considerably depending on the cation component as well as the occurrence of impurities and water content.*	-As electrolytes in batteries and solar cells -As unique solvents for electrochemical investigation, especially for transition metal complexes, which might be unstable in other media [3]

Other Uses

They are safe and stable electrolytes in a variety of electrochemical devices. Additionally, the unique properties of ionic liquids make them useful in numerous important areas. The table that follows lists some examples of each:

Electrochemical Uses	Additional Uses attributed to Unique Properties [9, 10]
-Electrochemical capacitors -High energy density batteries -Solar cells -Electrochromic windows	-Liquid-liquid extractions -Gas-liquid absorption -Liquid membrane separations -In nanomaterial technology -In the preparation of polymer-gel catalytic membranes -As stationary phases from chromatography -As matrices for mass spectrometry -As supports for the immobilization of enzymes -As liquid crystals -As heat transfer fluids

	-As azeotrope - (a mixture of two liquids that has a constant boiling point and composition throughout distillation) breaking fluids -Lubricants and plasticizers -As anticorrosion coatings -Electropolishing agents -Antimicrobial agents -In the generation of high-conductivity materials

Thermal Properties of ionic liquids

Thermal Stability

According to Endres, et al.,[11] ionic liquids can be thermally stable up to temperatures of 450 °C. The thermal stability of ionic liquids is limited by the strength of their heteroatom–carbon, and their heteroatom–hydrogen bonds, respectively.[11]

Melting Point

The thermal stability of the ionic liquid is also based upon the stability of the R-X anion type. The size, shape, and composition of the ions making up the ionic liquids affect the melting point by influencing the crystal packing ability and lattice energy of the ionic liquid.[12] The equation for calculating this energy is known as the Born-Lande, or Kaputinski equation and is shown below:

$$E_c = \frac{MZ^+Z^-}{4\pi\varepsilon_0 r}$$

Where E_c = Energy, coulombic

M = the Madelung constant, which is unitless

Z^+ and Z^- = the modulus* of the magnitude of positive and negative charges respectively

ε_0 = the permittivity of a vacuum = 8.854×10^{-12} F m^{-1}

r = internuclear distance between the ions (units = m)

*The modulus of a real number is its positive value. For example, if $Z^+ = Mg^{2+}$ then $Z^+ = 2(+)$ and if $Z^- = O^{2-}$ then $Z^- = 2(+)$ also.

The overall lattice energies depend upon the product of the net ionic charges, ion-ion separation, and the packing efficiency of the ions (this factor is reflected in the Madelung constant M in the Coulombic energy term).[12] *Low* melting points are preferred when the charges on the ions are +/-1 and when the size of the anions are large (this ensures that *r* is large), which will also reduce the overall charge *density*.

For a salt to melt at *room* temperature, the radius of the anion must be $\geq 3.4 - 4.0$ Å[12]. In general, the melting points of ionic liquids will *lower* with an increase in the *size* and *complexity* of the anionic and cationic components. This is due to a greater charge *delocalization* as well as the charge being sterically isolated. Additionally, lower melting points can be achieved by:

1. Increasing the size and charge differences
2. The presence of flexible substituents. These can contribute to
    a. Greater charge separation
    b. Disruption of lattice isotropy (having a physical property that has the same value when measured in different directions; not varying in magnitude according to the direction of measurement).
    c. The introduction of many rotational and vibrational modes of freedom

3. Inefficiencies in packing due to non-charge-bearing hydrocarbon groups.

All of these factors impart a *reduction* in salt lattice energies and small Coulombic interactions, lowering the melting point. Due to induced dipoles, which lead to hydrogen bonding, one *cannot* safely consider the contributions to thermal properties from the cation and anion in *isolation*.

Contributions by cations to the melting point

Size of the cation

Like the anionic component, increasing the size of the cation has the effect on lowering the melting point of ionic liquids. Increasing the length (size) of the R-groups, or alkyl substituents, also lowers the melting point due to the introduction of *additional rotational degrees of freedom*.

Interestingly, this trend is *not* straightforwardly predictable. For example, if the alkyl group substituent is between 1 – 8 carbons in length, the melting point does lower as the chain length increases due to reasons previously mentioned (destabilization of Coulombic packing). If a solid is to form, there is a trend towards glass formation, not crystallization. However, between a carbon chain length of 8 – 10 and beyond, the melting point *increases* due to increasing van der Waals forces between R-chains and increased structural ordering, leading to crystal formation.

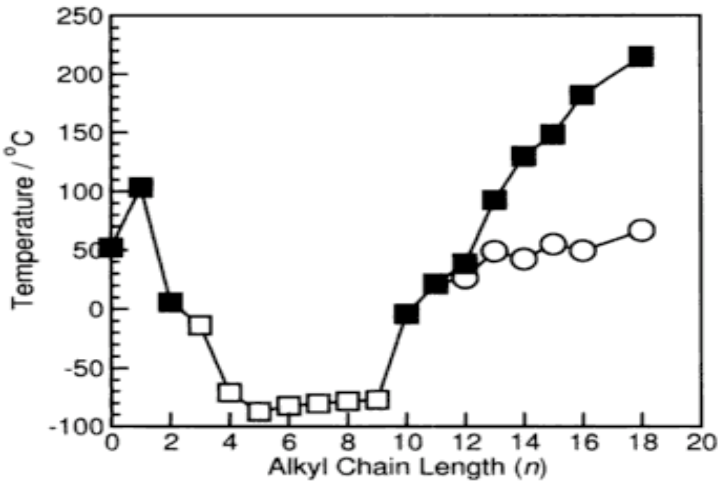

Figure 4. Melting points as a function of alkyl chain length for 1-alkyl-3-imidazolium tetrafluoroborate ionic liquids.[12]

True melting points are shown in solid black squares, and glass transitions with white squares. Note the trend toward decreasing melting points with n = 1 to n = 8, with an *increase* in melting points once n is greater than 8.

Contributions by the anion to the melting point

The dominant force that must be overcome between the ions in an ionic liquid to exist as a liquid is the Coulombic attraction between the oppositely charged particles.[13] This force is equated to charge and ion radius by Coulomb's Law:

$$F = \frac{q_1 q_2}{\varepsilon r^2}$$

The two factors that separate ionic liquids with relatively low melting points from those with high melting points:

1. The charge, q, on the ions is normally ±1
2. The size of the ions is large, which causes the distance separating them, r, to also be large.

Factor #2 leads to a larger separation of charge, which decreases Coulombic attraction, but that effect can be further augmented if the charge is delocalized over the volume of the anion. This dramatically reduces the charge density, further reducing the Coulombic attractive force.[13] Rogers et al, quantifies this factor experimentally and gives the following correlation of anion size to melting point:

From smallest anionic *r* to largest: Cl^- < [BF4$^-$] < [PF_6^-] < [$AlCl_4^-$] have respective melting points of 801ºC, 384 ºC, >200ºC, 185ºC, with a sodium cation.[13] Below we can see the effect of anion exchange on the [EMIM][X] ionic liquid, while holding the cation constant:

Table 2. Effect of anion on the melting point of ionic liquids.

Anion, [X]	Melting Point (ºC)	Anion, [X]	Melting Point (ºC)
Cl^-	87	[CH3CO2]-	ca. -45
Br^-	81	[SO4]- · 2H2O2-	70
I^-	79-81	[CF3SO3]-	-9
[BF^4]$^-$	15	[CF3SO2]-	-14
[$AlCl_4$]$^-$	7	[N(SO2CF3)2]-	-3
[GaCl4]-47	47	[N(CN)2]-	-21
[AuCl3]-	58	[CB11H12]-	122
[PF6]-	62	[CB11H6Cl6]-	114
[AsF6]-	53	[CH3CB11H11]-	59
[NO3]-	38	[C2H5CB11H11]-	64
[NO2]-	55		

Bagno, et al., states that with trihalide-based ionic liquids, DSC analysis reveals that the anion identity significantly influences the melting point.[14]

Effect of *branching* of the Alkyl Chain on the cation on melting points

Welton et al.,[12] tested three isomeric ionic liquids 1-butyl-3-methylimidazolium hexafluorophospahate [BMIM][PF_6], whose only difference was the degree of branching at the imidazolium ring (at the 3-position). The melting points and enthalpies increase as the degree of branching increases. This is explained by packing efficiency and atom density. As branching increases, the free-rotation volume *decreases*, and this allows for increased atom density as crystal packing efficiency is greater. They report the same observations for the two isomers of 1-propyl-3-methylimidazolium hexafluorophospahate [PMIM][PF_6].[12]

Table 3. The effect of alkyl substitution on melting points and heats of fusion.

N-substitution	Melting point (°C)	ΔH_{fusion} (KJ/mol)
n-butyl	6.4	31
sec-butyl	83.3	72
tert-butyl	159.7	83
n-propyl	40	-
Isopropyl	102	-

Symmetry

Symmetry correlates positively with melting point. As the symmetry of the ionic liquid increases, the melting point raises, as stacking can more readily occur. Examples of a cation with a high amount of symmetry include Na^+ and $[NMe_4]^+$. Low-symmetry ionic liquids exhibit lower melting points, lower packing efficiency, lower trend towards crystallization, and a higher tendency for glass formation on cooling as R-groups increase in length.

Conductivity of ionic liquids

Conductivity is defined as the ability of a substance to conduct electric current. It is the reciprocal of the more commonly known measurement, resistivity. Conductivity is positively correlated with temperature. Research by Endes et al.,[11] notes that ionic liquids have good ionic conductivities compared with those of organic solvents/electrolyte systems (up to ~10 mS cm^{-1}). Still, at room temperature their comparative conductivities are typically lower than those of concentrated aqueous electrolytes. This seems unexpected since ionic liquids are composed solely of ions. However, this can be explained by the mobility factor of the charges. Conductivity depends on the number of charge carriers but also on their mobility. Due to the large ions typically composing ionic liquids, their mobility is reduced, their viscosity is higher, and this leads to lower conductivities. Additionally, ion pair formation and/or ion aggregation would also lead to reduced conductivity. Since mobility and viscosity are inversely correlated, so are conductance and viscosity. As expected though, heating the ionic liquid will lower the viscosity and allow for greater charge mobility and hence, greater conductance.[11] Although Wasserschield,et al.,[14] reported that there is no clear relationship between conductivity and the anion, Endes et al.,[11] reported that anions which form hydrogen bonds, such as BF_4^- and PF_6^- have a pronounced effect on viscosity.[11,12] In general, conductivity is inversely correlated with viscosity since it reduces charge mobility.

However, it is not a guaranteed correlation. In a study of ionic liquids containing trihalide anions, Bango et al.,[15] indicates that [BMIm][Br_3] is the ionic liquid characterized by the highest conductivity even though it is the most viscous among the trihalide-based ionic liquids they investigated.[15] Their paper highlighted that the degree

of *ion dissociation*, as well as *ion shape* and *radius*, may play an important role in determining the transport properties, at least when we are talking about acidic imidazolium-based ionic liquids.[15] Conductivity values for various pyrrolidinium-containing ionic liquids at 25°C are given in table 4.

Table 4. Conductivity of pyrrolidine-based ionic liquids containing different anions.

Ionic liquids	Conductivity σ (mS/cm) ± 2%	Reference
[Pyrr][NO_3]	50.1	Me´rie`m A, et al.
[Pyrr][HSO_4]	6.8	"
[Pyrr][HCOO]	32.9	"
[Pyrr][CH_3COO]	5.9	"
[Pyrr][CF_3COO]	16.4	"
[pyrr][$C_7H_{15}COO$]	0.8	"

Viscosity of Ionic Liquids

Ionic liquids behave as Newtonian fluids – that is to say – they have been observed to have a constant viscosity regardless of strain. Examples of non-Newtonian fluids include emulsions and polymers, which will thin or thicken when strain is applied. When viscosities are determined experimentally, they are reported as either absolute viscosities (η) or kinematic viscosity (ν), the latter being normalized by factoring in the density of the fluid. Their relationship between these factors is

$$\eta/\rho = \nu$$

The unit of absolute viscosity η is the Poise (P, $g/cm^{-1}s^{-1}$), often reported in cP (centipoises). The unit for kinematic viscosity ν is the Stoke (St, cm^2s^{-1}), which is often reported in cSt (centistokes).

Compared to common organic solvents, ionic liquids are *more* viscous, ranging from 10 cP to more than 500 cP at room temperature. For a general comparison, water measures 0.890 cP, ethene glycol at 16.1, and glycerol at 934 cP.[12]

Factors affecting viscosity of ionic liquids include:

- Temperature (strongly dependent)
- Impurities (dramatic effect)
- Anion composition and anion size
- Identity of the cation (for non-haloaluminate ionic liquids)
- If the anion remains the same, the larger the R-group(s) or alkyl substituents, the higher the viscosity (for non-haloaluminate ionic liquids).
- In chloroaluminate ionic liquids, viscosity increases with increasing cation size.
    - Asymmetric alkyl substitution leads to lower viscosities.
- Finally, the addition of co-solvents reduces the viscosity

Bagno et al.,[15] reports that trihalide anions produce a particularly significant effect on the viscosity of corresponding ILs. He also states that changes in viscosity observed by changing the anion or cation of a given IL have been attributed primarily to an increase in *van der Waals forces*, although *hydrogen bonding* may also play some role.[18] Therfore, the combination of the increased anion size, more diffuse negative charge and decreased hydrogen bonding between anion and cation should result in a decrease in viscosity on going from Cl− to I− in the halide-based ILs. However, with trihalide anions, this trend was not observed. This implies that other factors come to bear on determining viscosity.

It was suggested that the potential for forming ion pairs or ion aggregates, depending on the anion size, strongly affects the electronic polarizability, viscosity and conductivity. Deviations from linearity have been observed (plotting ln g vs. ln r), suggesting that the viscosity alone does not account for the conductive behavior of these ILs.

Density of ionic liquids

Density is the property which is least impacted by temperature variations as well as by impurities. For example, a 5ºK change in temperature from 298-303 resulted in a mere 0.3% decrease in the density of an imidazolium-based ionic liquid studied by Perry whereas a 20 wt.% water impurity resulted in a only a 4% decrease in density.[23]

With imidazolium ionic liquids, cation-anion interactions and molecular packing are the parameters that determine the density. In these ionic liquids, the anion exerts a strong influence on the density, which decreases in the order PF_6^- > BF_4^- > $H_3CSO_3^-$. This shows that the more bulky PF_6^- anion is responsible for a more dense molecular packing.[17]

Ionic liquids in general are denser than water with values ranging from 1 to 1.6 g cm^3 and their densities *decrease* with *increase* in the length of the alkyl chain in the cation. For example, in ionic liquids composed of substituted imidazolium cations and $CF_3SO_3^-$ anion the density decreases from 1.39 g cm^{-3} for [EMIm] to 1.33 g cm^{-3} for [EEIm], to 1.29 g cm^{-3} for [BMIm] and to 1.27 g cm^{-3} for [BEIm][11] The densities of ionic liquids are also affected by the identity of anions. For example, the densities of 1-butyl-3-methylimidazolium type ionic liquids with different anions, such as BF_4, PF_6, TFA and Tf_2N are 1.12 g cm^{-3}, 1.21 g cm^{-3}, 1.36 g cm^{-3} , and 1.43 g cm^{-3} respectively.[20]

Electrochemical Properties of ionic liquids

As mentioned previously, ionic liquids have wide electrochemical windows. The electrochemical window of a substance is the voltage range between which the substance being analyzed is not electroactive (does not become oxidized or reduced).[18] These windows represent the voltage range under which they may therefore function as electrolytes before being oxidized or reduced. These windows also display the voltage at which oxidation occurs at the anode, and at reduction occurs at the cathode. Ionic liquids tend to have wide electrochemical windows compared to other solvents. Among ionic liquids, those containing the pyrrolidinium cation have particularly wide windows. However, it is important to note that trace impurities of water, oxygen, and the combination of both strongly affect the cathodic stability window of these ionic liquids.[18] limiting the potential window of ionic liquids.

Before being investigated as alternatives to conventional organic solvents, ionic liquids were being investigated for a variety of electrochemical applications.[9] Their high conductivity, wide electrochemical window (> 3.0 V), low melting points, low vapor pressure and thermal stability make them potentially useful as solvents in electrochemical devices, such as lithium and lithium ion batteries and capacitors. Also, their tendency to provide non-coordinating solvent media makes them attractive for electrochemical studies of transition metals.[9]

Ionic liquids based on pyrrolidinium cations and the TFSI− anion are considered to be the most promising for electrochemical applications, such as lithium batteries, due to their high conductivities and wide cathodic electrochemical windows[19]. The investigations of N-alkyl-N-methyl-pyrrolidinium TFSI ionic liquids have shown that

these ionic liquids have *wide* cathodic stability. However, it is important to note that trace impurities of water, oxygen, and the combination of both strongly affect the cathodic stability window of these ionic liquids.[19]

Miscibility with other solvents

Ionic liquids are highly-polar, yet often weakly-coordinating solvents. Their polarities fall between that of water and chlorinated organic solvents. Solvent studies show similar properties to short-chain alcohols and other polar, aprotic solvents (DMSO, DMF).[18]

To summarize, the miscibility of ionic liquids in water varies with cation substitution and anion types; coordinating anions lead to water-soluble ionic liquids, whereas the presence of large, non-coordination, charge diffuse anions generates hydrophobic ionic liquids.[18]

Uses for Ionic Liquids in synthesis and solvent extraction

Liquid–liquid extraction has often been a favored choice in process engineering for the development of separation processes. However, this process has traditionally employed an organic solvent with an aqueous solution as the two immiscible phases. The use of such media is problematic due to the toxicity, flammability, and volatility of these volatile organic compounds (VOCs), The costs of solvents are high and go beyond their direct value, as containment and disposal of spent extractants and diluents will attest.[20]

Recently, considerable interest has been manifest in the use of room temperature ionic liquids as solvents for industrial catalytic reactions. This approach appears to allow the controlled production of desired products from reactants with a minimum of waste

production through side reactions due to the tendency of ionic liquids to suppress conventional solvation and solvolysis phenomena.

The high solubilities of organic species, the practical absence of any significant vapor pressure (due to the prevalence of high coulombic forces), and the availability of air and moisture stable, water immiscible ionic liquids, may advocate such systems as being uniquely suited to the development of completely novel liquid-liquid extraction processes.[20] The use of ionic liquids for these purposes will assume increasing importance. Ionic liquids may in themselves be suitable, and indeed favorable, media for the design of novel liquid–liquid extraction systems.[20] In fact such systems may be uniquely suited to the development of completely novel liquid–liquid extraction processes.[20]

The link between ionic liquids and green chemistry is mostly related to the solvent properties of ionic liquids. One property that stands out above all others is the large liquidus range. The liquidus range is the span of temperatures between the freezing point and boiling point of a liquid. The consequence for green chemistry is that ionic liquids are the ultimate non-volatile (emphasis on *non*-) organic solvent, which is its other appealing feature from both a green and a safety standpoint. (Wilkes, 2002) No molecular solvent (other than molten polymers) comes even close to the low volatility of ionic liquids.

In liquid-liquid separations, "Once the organic compound is in the ionic liquid layer, it can be easily distilled since ionic liquids have negligible vapor pressure, and the ionic liquid can be recycled for future use. This separation process could possibly be used for removal of organic contaminates in wastewater treatment and ground soil contamination."[9]

Another timely discovery is the use of ionic liquids for the extraction of biofuels. Preliminary investigations using ionic liquids in these extractions show an enhancement of extractive *selectivities*.[21] The following attributes that make ionic liquids ideally suited as solvents for synthesis:

- They are good solvents for a wide range of both organic and inorganic species
- Although they are polar (due to their ionic nature), they are often composed of poorly coordinating ions, and therefore do not react chemically with any solute
- They are immiscible with a number of organic solvents and provide a nonaqueous, polar alternative for two-phase systems
- From an environmental point of view, ionic liquids are nonvolatile and allow volatile organic contaminants to be easily removed, but they themselves do not evaporate.[3]

Many conventional organic solvents tend to coordinate with the metal centers of catalysts, tying the metal ions up and making them less efficient catalysts. Since ionic liquids are nonvolatile liquids at ambient temperatures and are often composed of non-coordinating ions, they can be used as solvent media, catalysts and in some reactions, they function as both. They are a good substitute for the typical polar aprotic solvents because they dissolve both inorganic and organic materials.

Ionic liquids as electrolytes in solar cells and batteries

With our changing paradigm of energy production and usage, the use of solar energy may be an important energy source for the future. Qualities that make for a good

electrolyte include a wide electrochemical window, high thermal stability, wide liquid range, high conductivity and lack of vapor pressure. A good battery has an electrolyte that will not oxidize or reduce over the electrochemical window in which it is intended for use.[22] All of these requirements make ionic liquids good candidates for use in this capacity.

Lithium ion batteries are currently the best batteries yet produced. In a lithium ion battery, lithium ion (Li^+) is produced by the oxidation of a lithium atom (Li^0) at the anode and is then transferred back to the cathode. However, the Li^0 will react with the electrolyte, rendering the battery ineffective if the electrochemical window of the electrolyte is not large enough[22] Another condition met when considering a candidate for a useful electrolyte is the possibility that the battery may need to operate at elevated temperatures (higher than room temperature) so having an electrolyte that will not evaporate or degrade is also a very important factor. The thermal decomposition of many ionic liquids is above 350^0C – in fact the two being studied in this paper have thermal decomposition points above 400^0C. In addition, a highly conductive electrolyte is necessary in order to promote Li^+ movement through the electrolyte from the anode to the cathode in order to produce electricity.[22] Thermal conductivity rises in these ionic liquids as temperature rises. The very wide liquid range is also a beneficial aspect, as an electrolyte with a wide liquid range also allows for the solvation of a wide variety of inorganic, organic, and organometallic species which is very useful for battery applicaions.[12]

Use of ionic liquids in capacitors

In their paper tiltled "Carbon – Ionic Liquid Double-Layer Capacitors", authors A. Lewandowski, and M. Galinski study the effectiveness of a series of electrochemical capacitors, based on activated carbon powders (ACP, specific surface area 870 and 2600 m2/g) and ionic liquids as electrolytes. The ionic liquids consisted of 1-ethyl-3-methyl imidazolium ($EMIm^+$), 1-butyl-3-methyl imidazolium ($BMIm^+$) and 1-methyl-1-propyl pyrrolidinium ($BMPy^+$) cations, as well as of tetrafluoroborate, hexafluorophosphate and bis((trifluoromethyl)sulfonyl) imide anions. The capacity of the double layer formed at the interface between activated carbon and ionic liquid, obtained …is comparable to that characteristic for solutions of organic salts. The example given is of $(C_2H_5)_4NBF_4$, in organic solvents, such as acetonitrile or propylene carbonate. They state that the energy stored in a capacitor containing ionic liquids can be high, due to a broad practical electrochemical stability window of ca. 3 V. In addition, ionic liquids are characterized by negligible vapor pressure, which leads to systems containing no volatile component, and the resulting device may be regarded as environmentally friendly.

In fact, they give a "typical" cyclic voltammogram of a capacitor containing $EMIBF_4$ as an electrolyte, taken at a voltage range of ±1 V at a polarization rate of 5 mV/s. They go on to state that the voltammogram has an almost ideal rectangular shape, typical of the pure capacitive behavior of the device.[24]

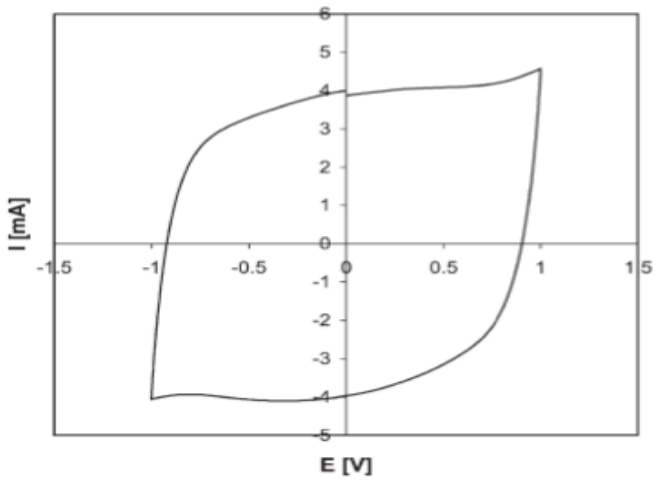

Figure 5. A “typical” cyclic voltammogram of a capacitor containing $EMIBF_4$ as an electrolyte

EXPERIMENTAL

Materials

1-butyl-1-methyl-pyrrolidinium chloride ($BMPy^+Cl^-$) was purchased from Emanuel Merck Darmstadt EMD at > 98% purity. Lithium bis(pentafluoroethanesulfonyl)-imide (LiBeti), (FC-130), was purchased from 3M Corporation and required no additional purification. Silver tetrafluoroborate ($AgBF_4$) was purchased from Alfa Aesar Co. and used as received. Deuterated acetone and acetonitrile (99.5+%) were purchased from Sigma-Aldrich. The viscosity standard used to calibrate the viscometers was a Certified Viscosity Reference Standard, N100 (lot #08301) from Cannon Instrument Company. Ferrocene was purchased from the Aldrich Chemical Company.

Synthesis of 1-butyl-1-methyl-pyrrolidinium BETI

1-butyl-1-methyl-pyrrolidinium BETI ($BMPyrr^+Beti^-$) was prepared by dissolving 25.481 g of $BMPy^+Cl^-$ in approximately 50 mL of deionized water. An equimolar amount of LiBeti (55.502g) was dissolved in deionized water (approximately 50 mL), and the two solutions were quantitatively transferred to a round-bottom flask and stirred for 3 days. Separation of the two layers was observed on the second day.

Using Pyrex 250 mL separatory funnels, the ionic liquid was washed three times with 20 mL portions of deionized water until testing negative for chloride with $AgNO_3$. The ionic liquid was then dried first on a low vacuum (10^{-2} mmHg), then on a high vacuum ((10^{-4} mmHg) at 80°C.

The identity of $BMPyrr^{+}Beti^{-}$ was confirmed by H^{+}NMR, ^{13}CNMR and ^{13}C DEPT 135 spectra. The spectra are displayed in the appendix. The amount of water was determined by coulometric Karl Fischer titration. For typical analysis, about 50 μL of sample was used.

Instrumentation and Methods of Analyses

Fourier transform infrared (FT-IR) spectra were obtained using a Mattson Genesis II FT-IR spectrometer (model number 960M0000) operating from 400 to 4000 cm^{-1}. The spectra were analyzed using Ominc Version 1.1 software. The ionic liquid sample was contained between two NaCl plates with a spacer of 0.025 mm thickness.

The TGA data was obtained using a Perkin Elmer Series 7 Thermal Analysis System. Using nitrogen gas, the ionic liquids were both subject to a temperature ramp beginning at 30.0 ºC and ending at 500 ºC. The rate of heating was also the same for both liquids, that being 10.0 ºC/min. The average weight of the samples was 15.9 mg.

FT-NMR spectra were obtained using a Bruker 300 MHz FT-NMR spectrometer. Samples were dissolved in deuterated acetone as the solvent. HNMR, ^{13}CNMR, and ^{13}C DEPT-135 spectra were obtained. These spectra are displayed in the appendix.

Differential Scanning Calorimetry

With differential scanning calorimetry, heat absorption measurements are made as a function of temperature. A reference, whose heat capacity is well known, is used in tandem with the sample under analysis. The sample and the reference are heated at the same rate. However, more heat will be required for the sample than the reference if it

undergoes an endothermic process. Less heat will be required for the sample when it undergoes an exothermic process than would the reference. These processes will generate a difference in heat flow between the sample and the reference, which the DSC can measure as heat absorbed/released.

Although the typical graph for a DSC analysis is plotted as a function of heat flux verses time, or versus temperature, a peak that is endothermic may appear as a positive peak on one instrument, and as a negative peak on another, depending on the type of DSC employed. For this study, a sample weight of 15.635 g of 1-butyl-1-methyl-pyrrolidinium BETI was placed in a hermetically-sealed pan, and weighed on a Perkin-Elmer Micro-balance (model # 302-0051). A typical DSC plot is given in Figure 6 below.

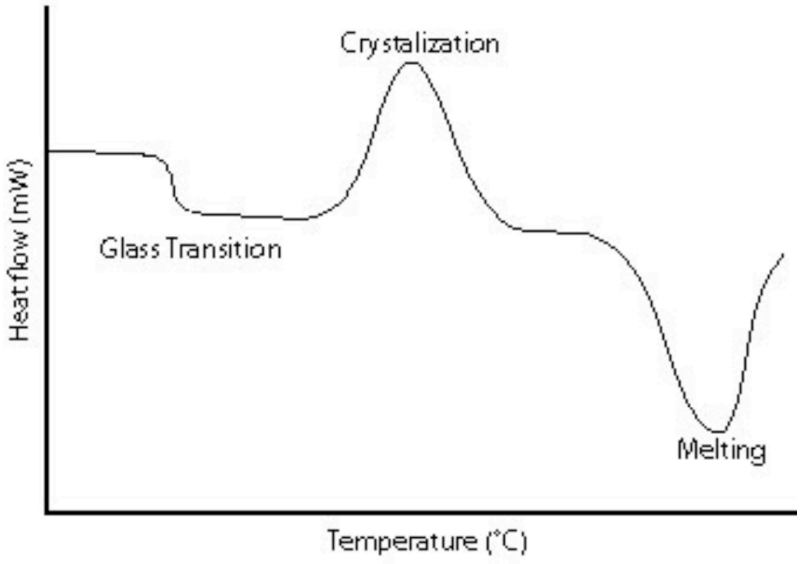

Figure 6. The features of a DSC curve.

Absorption and Desorption of Water by the ionic liquid BMPyrrBeti

To measure moisture content of the ionic liquid (BMPyrrBeti), a 2 mL sample was first placed into a clean, dry conical vial. The equipment used was the same that used to test BMImBeti. The vial was placed into the polymer glove box (Coy Laboratory Products) equipped with a Model 514 Automatic Humidity Controller from Electro Tech Systems was. The humidity was raised to 60% and kept at that humidity by adding water to the controller when necessary. A Denver Instruments Coulometric Karl Fischer Titrator (Model 260) was used to determine the amount of H_2O in the ionic liquid. The titrator was calibrated with Hydranal standard containing 100 ppm. Samples of ~ 50 µL were injected with a glass syringe using a stainless steel needle into the titrator., which had been cleaned and dried in an oven at 60-80 ºC prior to use. Several titrations were performed and the average values were taken when consecutive measurements were within 100 ppm. The samples were inverted several times during the titration process to mix the liquid, but the samples were not stirred.

Measurements were taken at various intervals and plotted as a function of water content (ppm) of water versus time (min). For the desorption process, the humidity was lowered to 6% and the procedure was repeated.

Conductivity

Conductivity was measured using an Oakton digital conductivity meter (model WD-35607-10) and a conductivity electrode (microelectronics Inc. (16-900). The ionic liquid was placed in a conductivity cell, which was designed to house the conductivity probe (Figure 7).

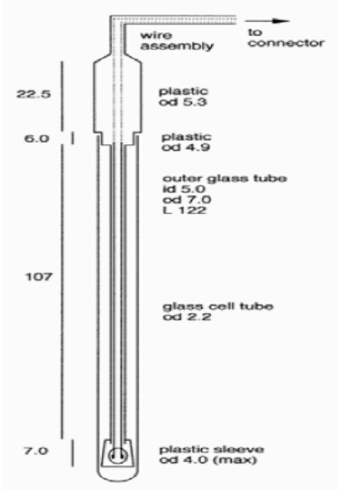

Figure 7. The Microelectronics Inc. conductivity electrode (#16-900).

This system was then placed in a constant temperature water. Conductivity readings were taken at various temperatures.

The conductivity cell was calibrated with 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 M KCl at different temperatures. A plot of literature values of k (for 0.1M KCl) vs. temperatures are given in Figure 8 and shown in Table 5.

Table 5. Accompanying kappa values (mS/cm) for KCl at specified temperatures.

T	K	T	K
15	1.1415	23	1.3536
16	1.1675	24	1.3808
17	1.1936	25	1.4081
18	1.2199	26	1.4356
19	1.2464	27	1.4632
20	1.2730	28	1.4909
21	1.2997	29	1.5187
22	1.3266	30	1.5467

T = Temperature (°C)
K = Conductance (mS cm^{-1})

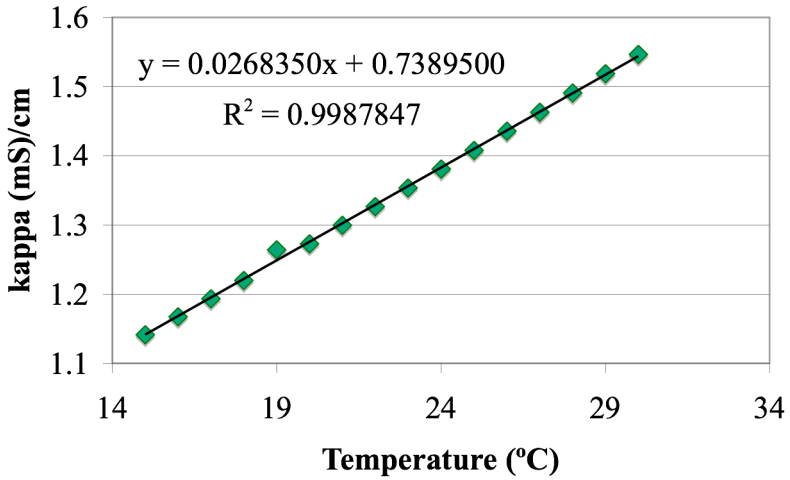

Figure 8. A plot of k versus temperature for 0.1 M KCl.

Because the kappa values in the accompanying literature were all correlated to temperatures in whole-number increments, the previous plot allowed the determination of kappa values at temperatures that were not provided for in the accompanying literature (ex.: 19.3 ºC vs. 19.0 ºC).

Once the temperature-adjusted kappa values were obtained, a table was built in preparation for the generation of a plot to obtain the cell constant. The table is shown below:

Table 6. Conductance and kappa values of BMPyrrBeti at various molarities.

[KCl]	ºC	Conductance (mS)	Adj kappa (ms/cm)	d/A
0.01	19.3	1.34	1.26	1.1251
0.02	18.8	2.63	2.49	
0.04	18.7	4.85	4.96	
0.06	18.8	7.30	7.46	
0.08	18.8	9.45	9.95	
0.1	18.8	11.10	12.43	

Using the formula k = L(d/A), where K is kappa (mS cm^{-1}), L is the measured conductivity in mS, and d/A is the cell constant (cm^{-1}), also known as Θ, a plot of K vs L was made to obtain the cell constant Θ, (d/A).

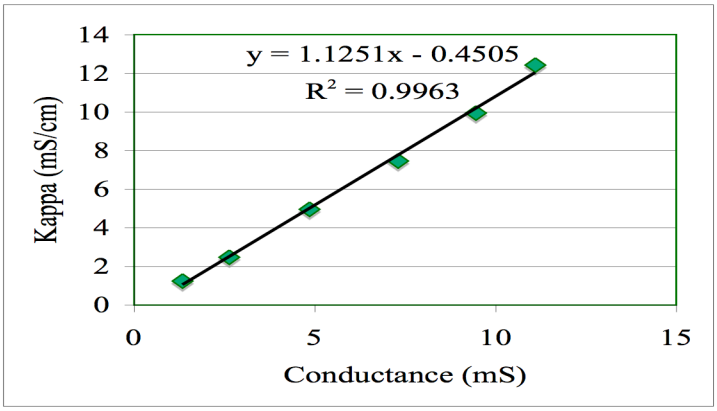

Figure 9. Plot of kappa versus conductance to obtain Θ, (d/A).

Once the cell constant (d/A) had been determined from the slope of the line in Figure 7, it was multiplied by the conductance measured at each temperature point to arrive at the k (kappa) values, which represent the actual conductivity of the ionic liquid in mS/cm.

Cyclic voltammetry

The cyclic voltammograms were measured using a Princeton Applied Research Potentiostat/Galvanostat (Model 173) equipped with an EG&G Parc. Universal Programmer (Model 175). The analog data was converted to digital data using a MacLab/4 Analog Digital Instruments interface. The data was recorded digitally using Scope V3.1 software, running on a Macintosh operating system. Approximately 1 mL of ionic liquid was placed into a miniature electrochemical cell. A glassy carbon electrode

was used as the working electrode, a Ag|AgCl electrode served as the reference electrode, and a Pt wire as a counter electrode.

Electrochemistry of Ferrocene

As with cyclic voltammetry, a glassy carbon electrode was used as the working electrode, a Ag|AgCl electrode served as the reference electrode, and a Pt wire as a counter electrode. Sensitivities were set at 10 μA/V.

To study the electrochemical properties of a transition metal in BMPyrrBeti, 10.4 mg of ferrocene (Cp_2Fe/Cp_2Fe^+) was dissolved into one gram of the ionic liquid. The molarity of the solution was calculated to be 6.05×10^{-2} M. The sample was run at two temperatures to compare the change in the diffusion coefficient as a function of temperature. The first experiment was conducted at 25.4 ºC. Using cyclic voltammetry, the sample was subjected to varying scan rates of 20, 50, 100, 200, and 500 mV/s. After measuring the anodic peak current, $I_{p,a}$, and applying the Randles-Scevik equation, the diffusion coefficient was determined.

Density

Density of the ionic liquid was measured using a picnometer standardized to 2 mL at 25ºC. For calibration purposes, the density of water was measured at 20, 30, 40 and 50 ºC. These values were then compared to standard values.

In order to measure the density of the ionic liquid, the sample was placed into the flask up to the mark, sealed, and placed into a temperature bath for ten minutes to allow the temperature to equilibrate. The flask was then removed from the bath, dried, and

immediately weighed. The sample was measured at least three times to determine the average value.

Viscosity

Viscosity measurements were taken at 20 ºC, 30 ºC, 40 ºC, and 50 ºC using a Cannon 300 Cannon-Fenske Routine glass viscometer manufactured by Cannon Instrument Company (Figure 8). The viscometer was calibrated using a Certified Viscosity Reference Standard, N100 (lot #08301) from Cannon Instrument Company (Table x).

Figure 10. A Cannon-Fenske viscometer used for measuring viscosity.

Table 7. The calibration data for the Cannon 300 Cannon-Fenske Routine glass viscometer measured at 20 ºC.

Time (s)	Kinematic Viscosity (mm^2/s)	Viscometer Constant (mm2/s2)
785.46	315.7	0.4019
762.21	315.7	0.4142
768.41	315.7	0.4108
772.03	315.7	0.4089
Average		0.4090 +/- 0.0001

Table 8. The calibration data for the Cannon 300 Cannon-Fenske Routine glass viscometer measured at 50 ºC.

Time (s)	Kinematic Viscosity (mm^2/s)	Viscometer Constant (mm^2/s^2)
148.30	60.3	0.4066
148.45	60.3	0.4062
150.00	60.3	0.4020
148.92	60.3	0.4049
Average		0.4049 +/- 0.0003

In order to measure the kinematic viscosity, the sample was brought to a constant temperature in a water/isopropanol bath. After 10 minutes, the sample was removed from the bath and the time it took for the ionic liquid to flow through the viscometer was measured immediately, performing at least three measurements. For higher temperatures, the viscometer was kept in the water bath as much as possible to ensure the ionic liquid was kept at a constant temperature. The time was then multiplied by the viscometer constant to get the kinematic viscosity. For example:

$$119.85 \text{ s} \times 0.4049 \text{ mm}^2/\text{s}^2 = 241 \text{ mm}^2/\text{s} \text{ (241 Stokes).}$$

Absolute viscosity, η, was determined by multiplying the kinematic viscosity by the density of the sample as shown below.

$$241 \text{ mm}^2/\text{s} = 2.41 \text{ cm}^2/\text{s}$$

The kinematic viscosity was then multiplied by the density of the sample to arrive at the absolute viscosity, η:

$$2.41 \text{ cm}^2/\text{s} \times 1.086 \text{ g/cm}^3 = 2.612 \text{ g/cm s (2.612 Poise, } \eta \text{)}$$

$$2.612 \text{ Poise} \times 100 = 261.2 \text{ centiPoise (c}\eta\text{)} = 261.2 \text{ mPa s.}$$

III. RESULTS AND DISCUSSION

In this work, a new type of ionic liquid containing the pyrrolidinium cation was synthesized and characterized. Its physical and electrochemical properties were investigated and compared to the properties on an analogous ionic liquid containing the imidazolium cation (Figure 11).

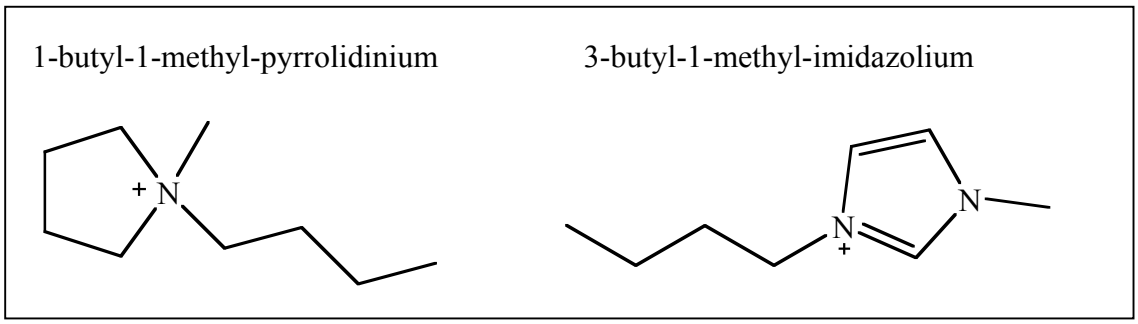

Figure 11. The structure of 1-butyl-1-methyl-pyrrolidinium and 3-butyl-1-methyl-imidazolium - the cationic components of the two ionic liquids compared in this study.

1-butyl-1-methyl-pyrrolidinium Beti was prepared from $BMPy^+Cl^-$ by metathesis with LiBeti in water. The reaction is shown below in Figure 12. After the reaction was complete (in 3 days time), two layers formed. The ionic liquid layer was separated in separatory funnels and washed several times with 20 mL portions of deionized water until all Cl^- ions were removed. Silver nitrate was used to test for traces of cloride ion.

The ionic liquid was then dried first on a low vacuum (10^{-2} mmHg), then on a high vacuum (10^{-4} mmHg) at 80 ºC. The water content of the ionic liquid was measured at certain time intervals using the Karl Ficher Coulometric titrator as described in the experimental section. After drying BMPyrrBeti contained about 56 ppm of H_2O.

1-butyl-1-methyl-pyrrolidinium chloride ($BMPy^+Cl^-$)

Lithium bis((pentafluoroethane)sulfonyl)imide (Li^+Beti^-)

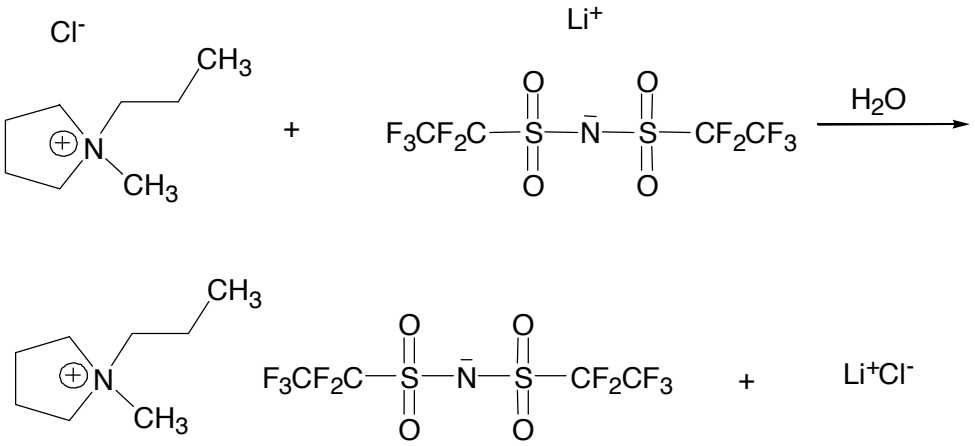

Figure 12. Metathesis reaction of 1-butyl-1-methyl-pyrrolidinium chloride with Lithium bis((pentafluoroethane)sulfonyl)imide (LiBeti).

The corresponding ionic liquid, (BMImBeti), was synthesized from BMI^+Cl^- and Li^+Beti in a similar reaction. 1-butyl-3-methyl-imidazolium chloride was synthesized in a pressure bottle by reaction of 1-chloro-butane with N-methyl-imidazole. Typically, a 1% excess of 1-chlorobutane was added to previously distilled N- methyl-imidazole and allowed to react for approximately 10 days at 45-50 ºC. A longer reaction time was required due to the nature of the chloroalkanes; a longer alkyl chain will decrease the reactivity of the chloroalkane.[22]

The synthesis involved the formation of 1-alkyl-3-methylimidazolium chloride by the reaction of the corresponding alkyl chloride with N-methylimidazole as shown below in Figure 13:

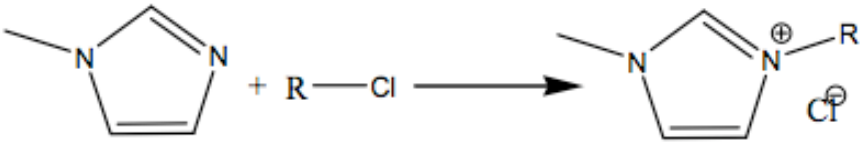

Figure 13. The synthesis of the imidazolium cation.

The second step in the formation of the ionic liquids involved the replacement of the chloride ion with the Beti- anion in a metathesis reaction as shown in figure 13:

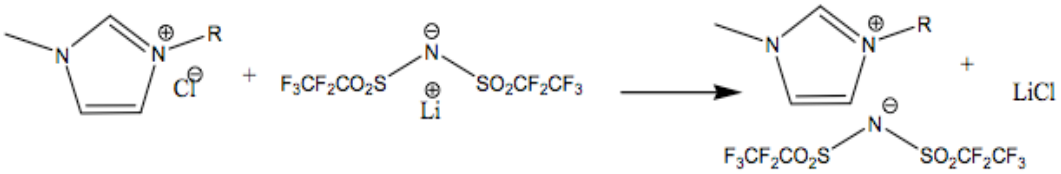

Figure 14.The general anion metathesis reaction for imidazolium cation.

The complete mechanism for the specific ionic liquid BMImBeti is shown in Figure 15 below:

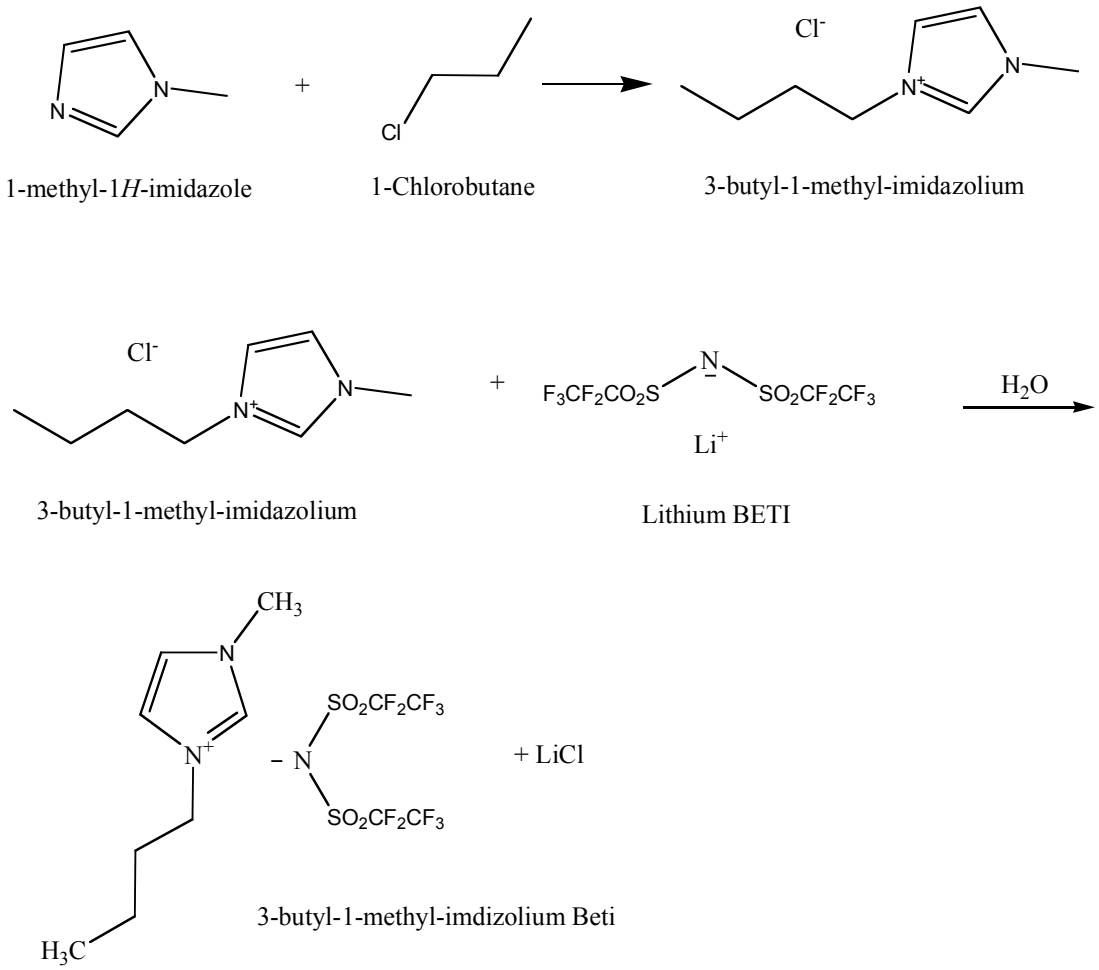

Figure 15. Stepwise synthesis of BMImBeti from imidazole.

Absorption and Desorption of Water

As mentioned previously[22] , ionic liquids containing the imidazolium cation absorb H_2O when exposed to a humid environment, although some ionic liquids do not mix with water. The absorption of water is reversible, i.e., upon lowering the humidity, desorption

of H_2O occurs. The concentration of water absorbed by ionic liquids levels off after several hours. The amount of absorbed water by the ionic liquid was a function of the length of the alkyl groups on the imidazolium cation as well as the kind of anion. In this work, we have investigated how the change of cation influenced the absorption and desorption of water by the ionic liquid. The water absorption curve obtained for BMPyrrBeti is shown in Figure 16 and given in Table 9.

For comparison, the water absorption curve for BMImBeti is shown in Figure 17. Figure 17 compares the H_2O absorption for both BMPyrrBeti and BMImBeti. Figures 16 and 18 show that BMPyrrBeti reaches saturation (2500 ppm H_2O), after which no more absorption of water takes place. Figure 17 and 18 show that BMImBeti, in comparison to BMPyrrBeti, absorbs H_2O much faster and reaches saturation after ~ 260 minutes. The imidazolium-based ionic liquid, BMImBeti absorbs significantly more water (~ 3500 ppm), than the pyrrolidinium-based ionic liquid, BMPyrrBeti (2500 ppm).

Table 9. Water absorption for BMPyrrBeti as a function of time at 60% humidity.

Time (min)	ppm H2O	Time (min)	ppm H2O
0.0	34.6	481.0	1214.0
67.0	90.3	1306.0	2051.0
123.0	316.3	2661.0	2445.7
184.0	660.9	7067.0	2456.5
278.0	926.4		

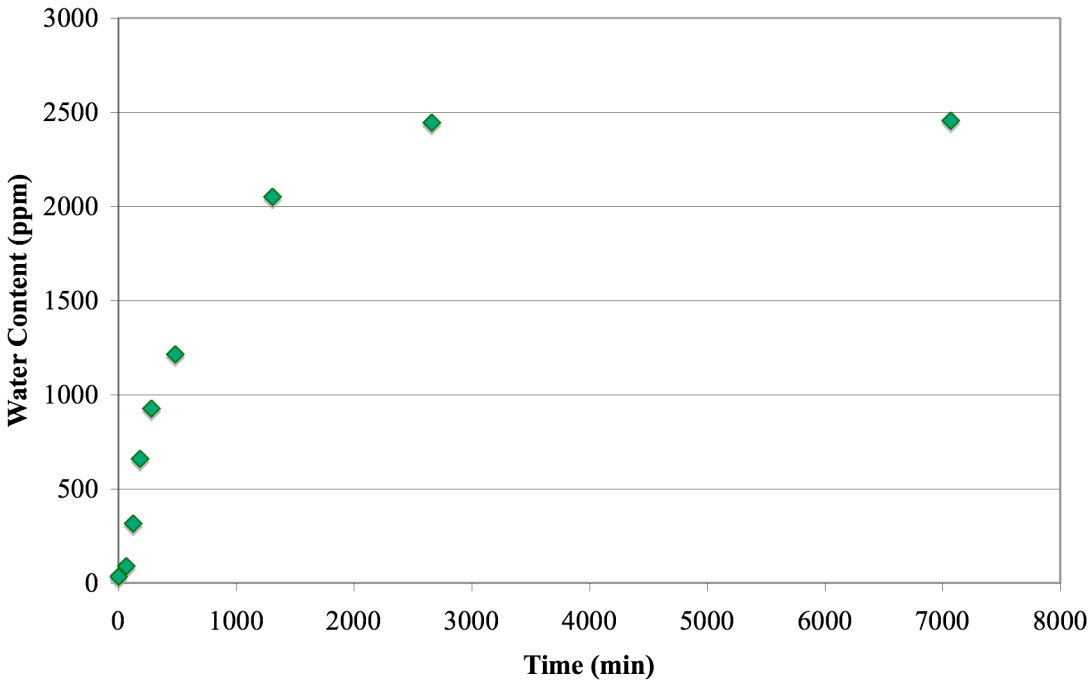

Figure 16. Water absorption by 1-butyl-1-methyl-pyrrolidinium BETI

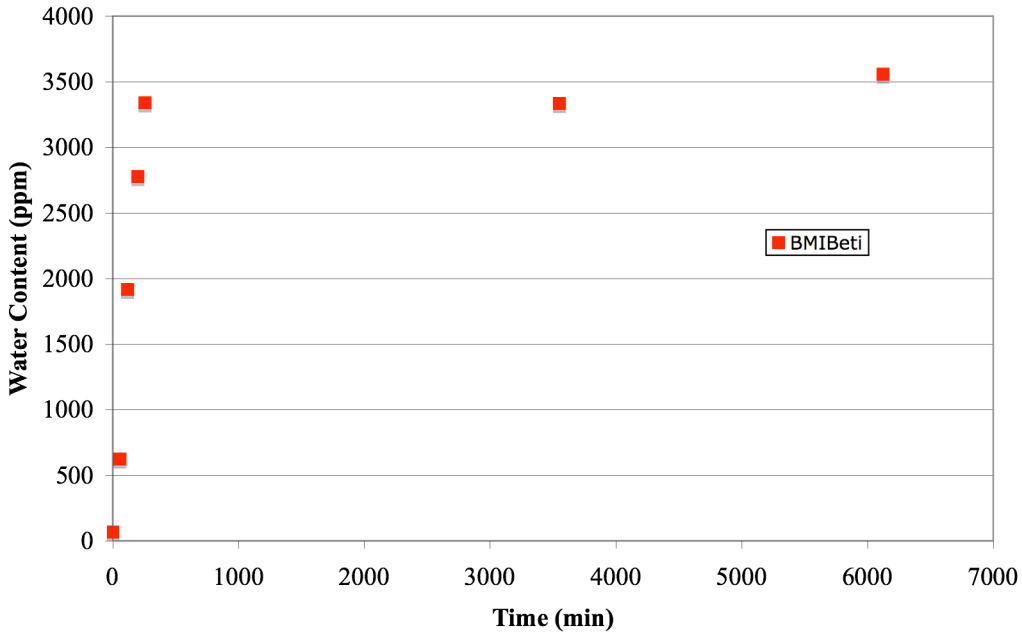

Figure 17. Water absorption by 3-butyl-1-methyl-imidazolium-BETI

Table 10. The maximum amount of water absorbed at 60% humidity by both ionic liquids.

Ionic Liquid	Maximum Water Content (ppm)
BMPyBeti	2500
BMIBeti	3600

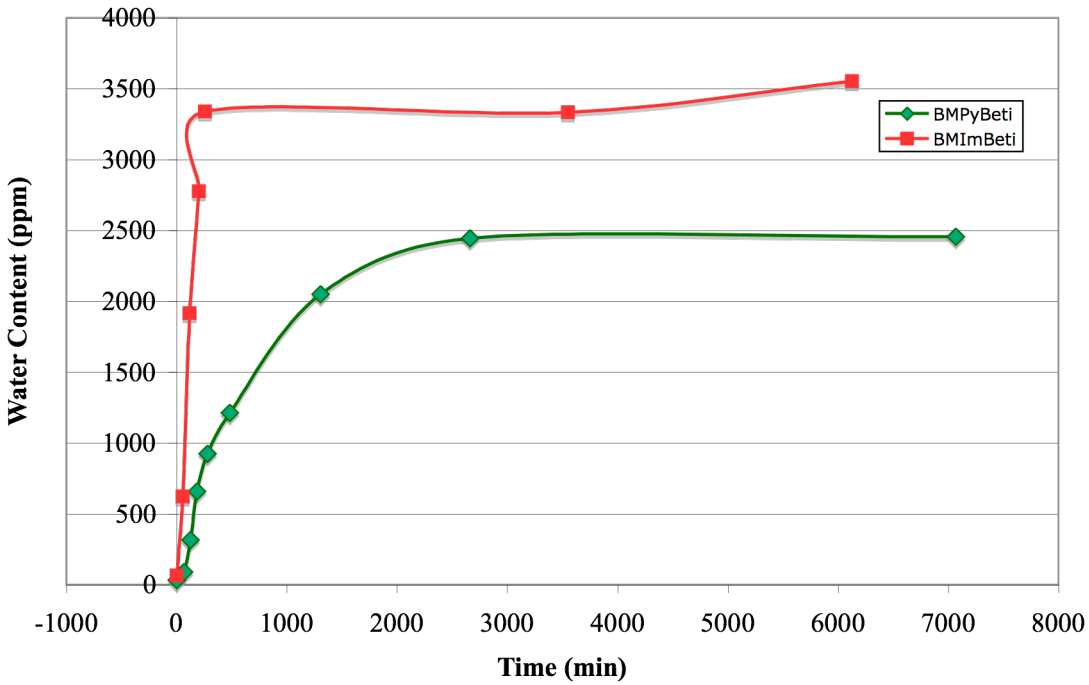

Figure 18. Comparison of Water absorption by both ionic liquids.

It can also be noted that the imidazolium-based ionic liquid reached its maximum water saturation point at 256 minutes, whereas the pyrrolidinium-based ionic liquid took 2661 minutes to reach that point. In other words, the imidazolium-based ionic liquid reached its maximum water saturation point about ten times sooner than the pyrrolidinium-based ionic liquid.

The water desorption studies found that ionic liquids will desorb water when exposed to a less humid (~ 6%) environment.[21] In a second experiment, the ionic liquids, after absorbing water at 60% humidity level, were exposed to a 6% humidity environment (Figure 19). The imidazolium-based ionic liquids desorbs water at a faster rate, but have potentially much more water to lose even when exposed to the same humidity level as the pyrrolidine-based ionic liquid. The level of water absorption is lower with 1-butyl-1-methyl-pyrrolidinium BETI, but the rate of water desorption appears to be slower than 1-butyl-3-methyl-imidazolium BETI (Figure 20 and 21).

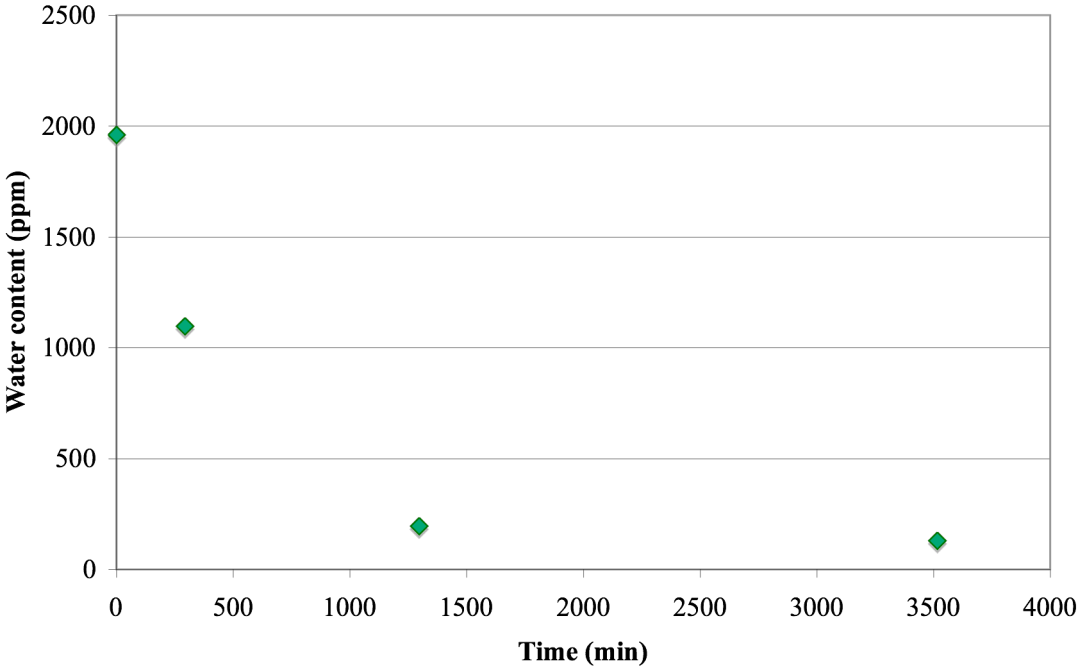

Figure 19. Desorption of water from BMPyrrBeti

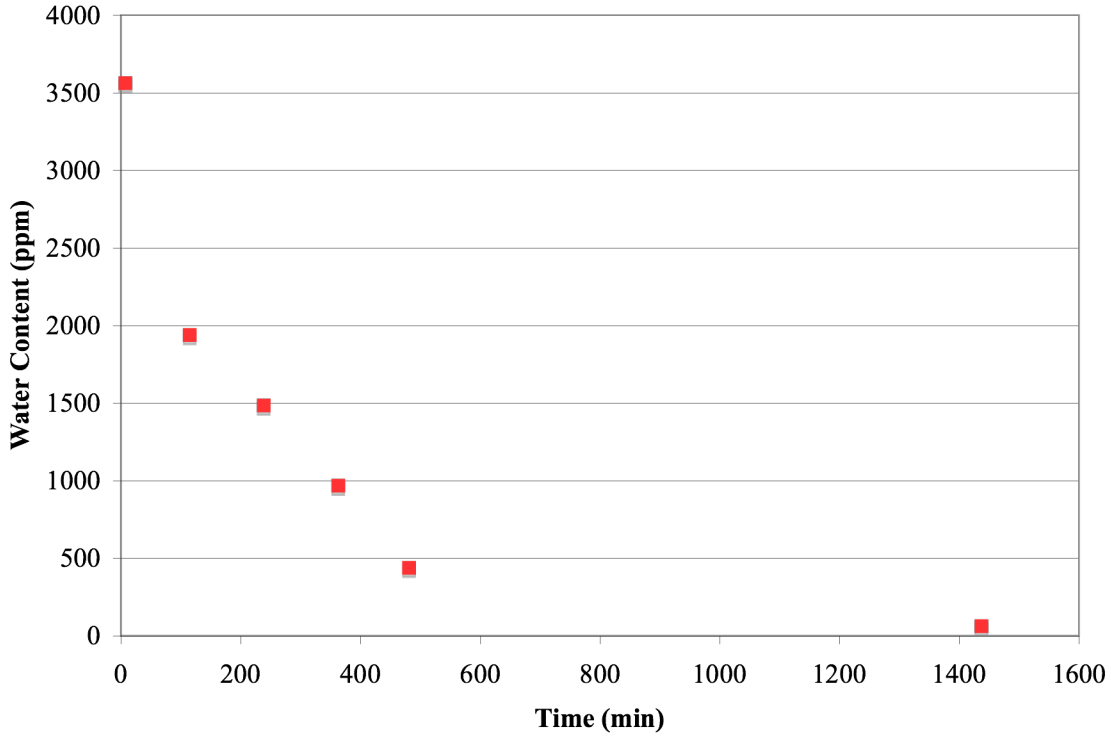

Figure 20. Desorption of Water BMImBeti

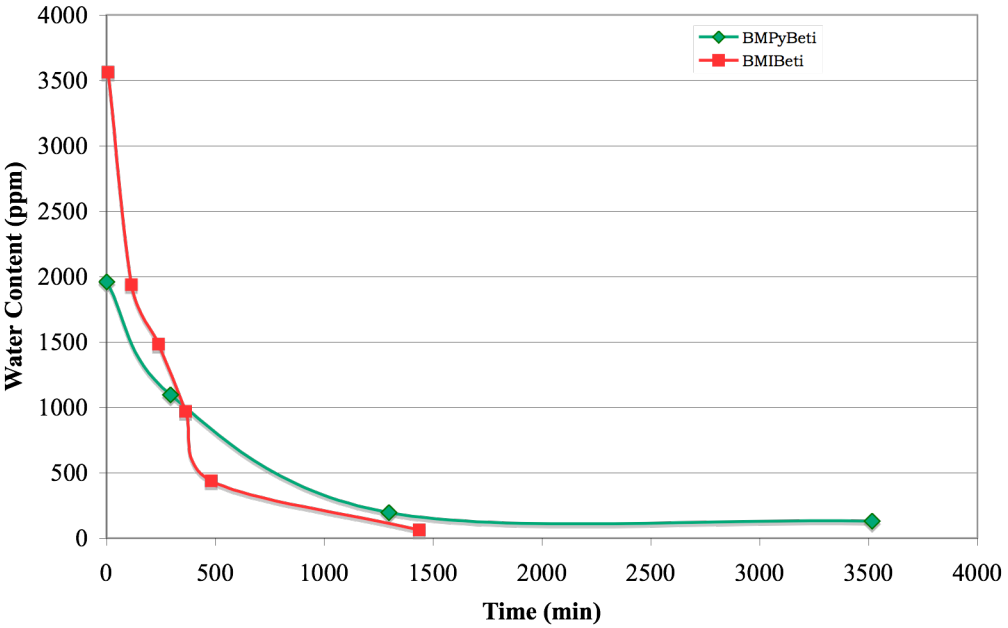

Figure 21. Comparison of water desorption by 1-butyl-1-methyl-pyrrolidinium BETI and 3-butyl-1-methyl-imidazolium-BETI

Water Absorption Studies by Infrared Spectroscopy

Fourier-transform infrared spectroscopy was employed to determine the molecular *state* of the H_2O absorbed by the ionic liquid. It was previously found in this laboratory that when the ionic liquid contains a small amount of water, it will be present in the monomeric form only[22]. When the concentration of water increases, water will polymerize by forming H-bonds, and this will become evident in the IR spectra. The spectral signature for this phenomenon are in two areas - between 1595 – 1650 cm^{-1} and between 3000 – 3800 $cm^{-1.}$ The first frequency range corresponds to the bending mode of monomeric water, and the second range corresponds to the stretching bands of monomeric water. Of the latter, the left-most peak displays asymmetric stretching, and the right-most peak, symmetric stretching.

A broad peak will form if the water begins polymerizing, as is seen when hydrogen bonds form. Figure 21 below displays such a spectra. The ionic liquid is HMIBeti (1-hexyl-3-methylimidazolium Beti), and polymerization is seen in the circled area:

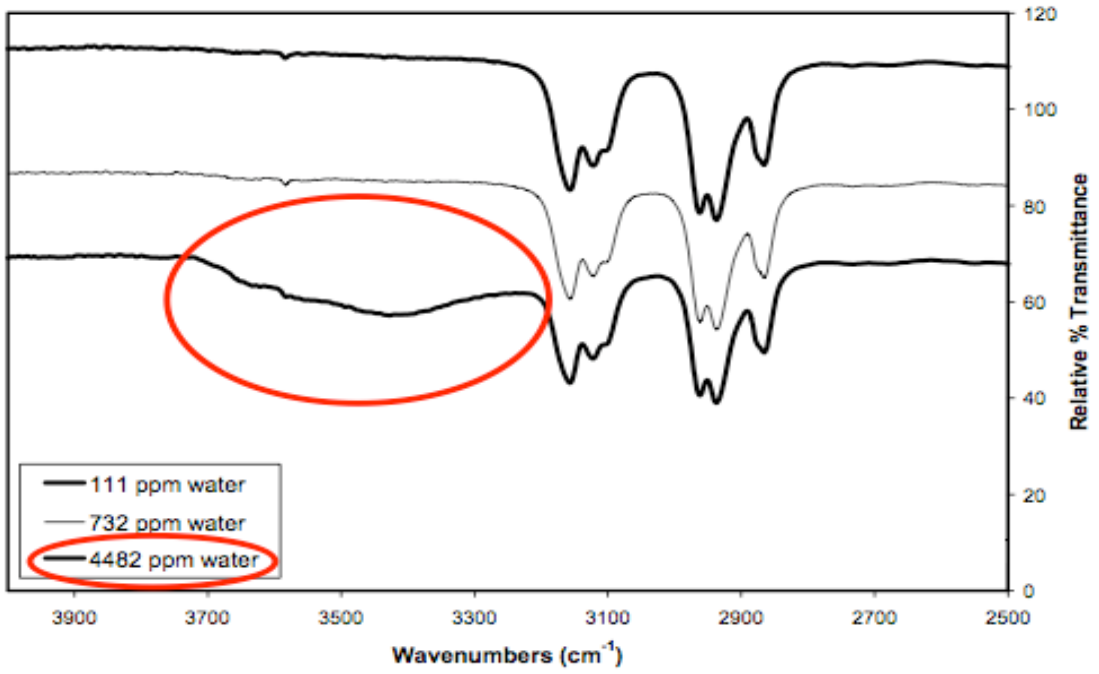

Figure 22. Infrared spectra of 3-butyl-1-methyl-imidazolium-Beti containing different amounts of water.

1-butyl-1-methyl-pyrrolidinium BETI does not absorb water readily. The IR spectra of BMPyrrBeti containing different amounts of water are shown in Figure 23. The spectra display two sharp bands in the range 3500 – 3700 cm^{-1} which correspond to symmetric and anti-symmetric stretching of monomeric H_2O. The spectra clearly show that water dissolved in BMPyrrBeti is in monomeric form only.

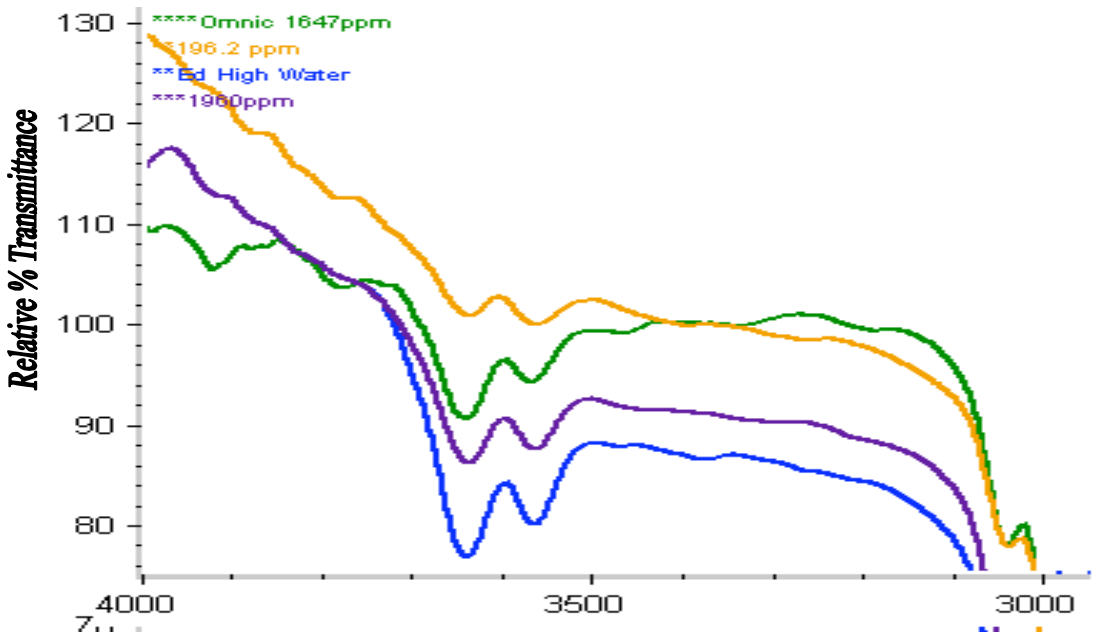

Figure 23. Absorption of water by 1-butyl-1-methyl-pyrrolidinium Beti.

Density

The density data for BMPyrrBeti and BMImBeti within the temperatures range of 20 ºC and 50 ºC are given in Table 12 and shown in Figure 24. At all temperatures, the density of BMPyrrBeti was smaller by about 0.42 g/mL than the density of the corresponding imidazolium ionic liquid. In both cases, as the temperature increased from 20 ºC to 50 ºC, the density decreased by about 0.2 g/mL.

Table 11. Density values for BMPyrrBeti and BMImBeti at different temperatures (in g/mL).

Ionic Liquids	H_2O (ppm)	20ºC	30ºC	40ºC	50ºC
BMPyrrBeti	49.4	1.086	1.081	1.07 6	1.065
BMImBeti	80.3	1.507	1.508	1.499	1.482

Table 12. Comparison of densities of BMPyrrBeti and BMImBeti at different temperatures as a percent of each other.

% ρ @ ºC	20ºC	30ºC	40ºC	50ºC
BMPyrrBeti	72.06	71.69	71.77	71.85
BMImBeti	138.8	139.5	139.3	139.2

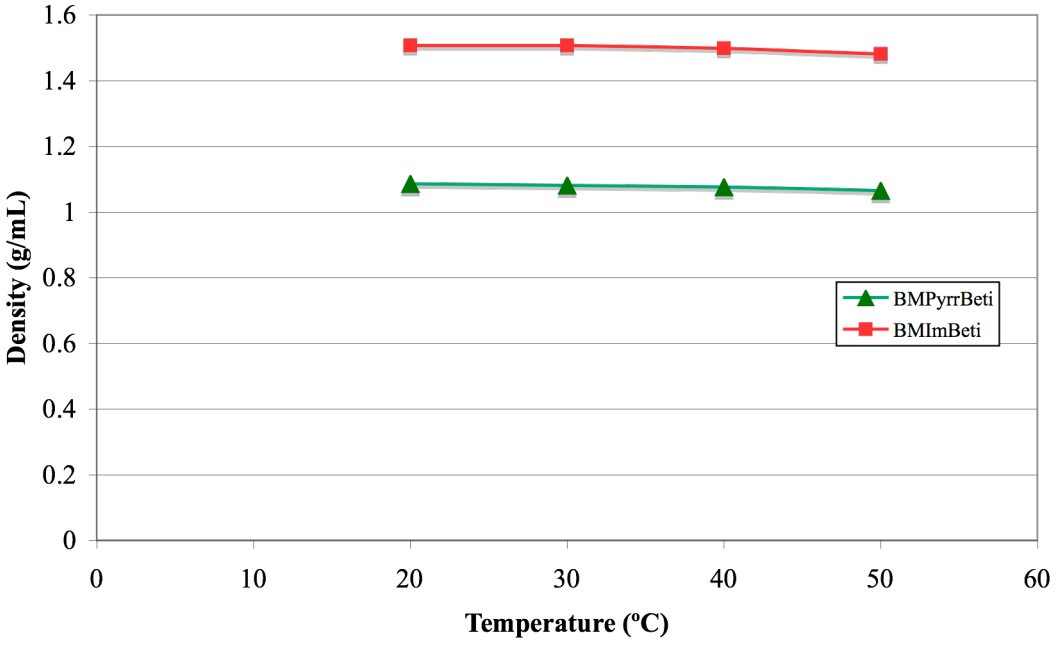

Figure 24. Densities of 1-butyl-1-methyl-pyrrolidinium BETI and 1-butyl-3-methyl-imidazolium as a function of temperature.

Viscosity

The kinematic (ν) and absolute (η) viscosities of 1-butyl-1-methyl-pyrrolidinium BETI were experimentally measured and compared to those for 3-butyl-1-methyl-imidazolium-BETI. 1-butyl-1-methyl-pyrrolidinium BETI was found to exhibit higher kinematic viscosities than 3-butyl-1-methyl-imidazolium-BETI at corresponding temperatures.

Table 13. Kinematic viscosity (ν) values for the two ionic liquids at different temperatures (in mm^2/s).

Ionic Liquids	H_2O Content	20ºC	30ºC	40ºC	50ºC
BMPyrrBeti	49.4	240.55	134.73	77.04	48.53
BMImBeti	80.3	101.4	76.2	36.91	24.89

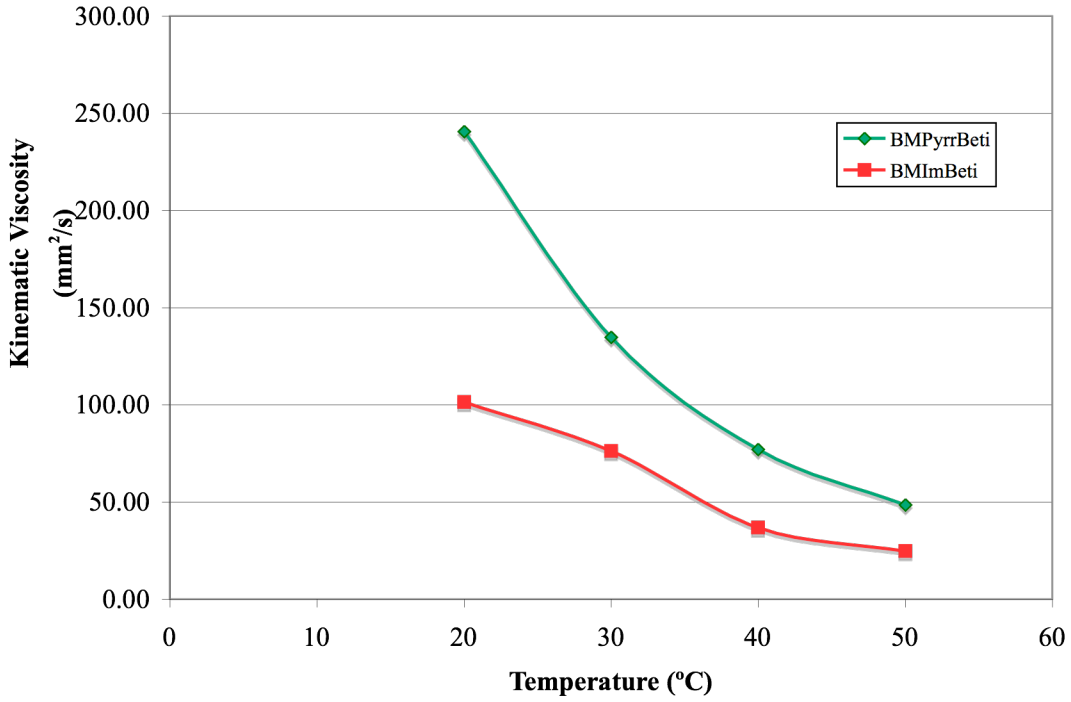

Figure 25. Kinematic Viscosities (ν) of 1-butyl-1-methyl-pyrrolidinium Beti and 1-butyl-3-methyl-imidazolium Beti.

Absolute viscosities (η) are obtained by multiplying kinematic viscosities by the density of the ionic liquid at a specified temperature. Absolute viscosities for 1-butyl-1-methyl-pyrrolidinium BETI are also higher than those for 3-butyl-1-methyl-imidazolium-BETI at corresponding temperatures.

Table 14. Absolute viscosity (η) values for the ionic liquid series at different temperatures (in mPa·s).

Ionic Liquids	H_2O Content	20ºC	30ºC	40ºC	50ºC
BMPyrrBeti	49.4	261.22	145.65	82.88	51.67
BMImBeti	80.3	152.1	114.4	55.32	36.88

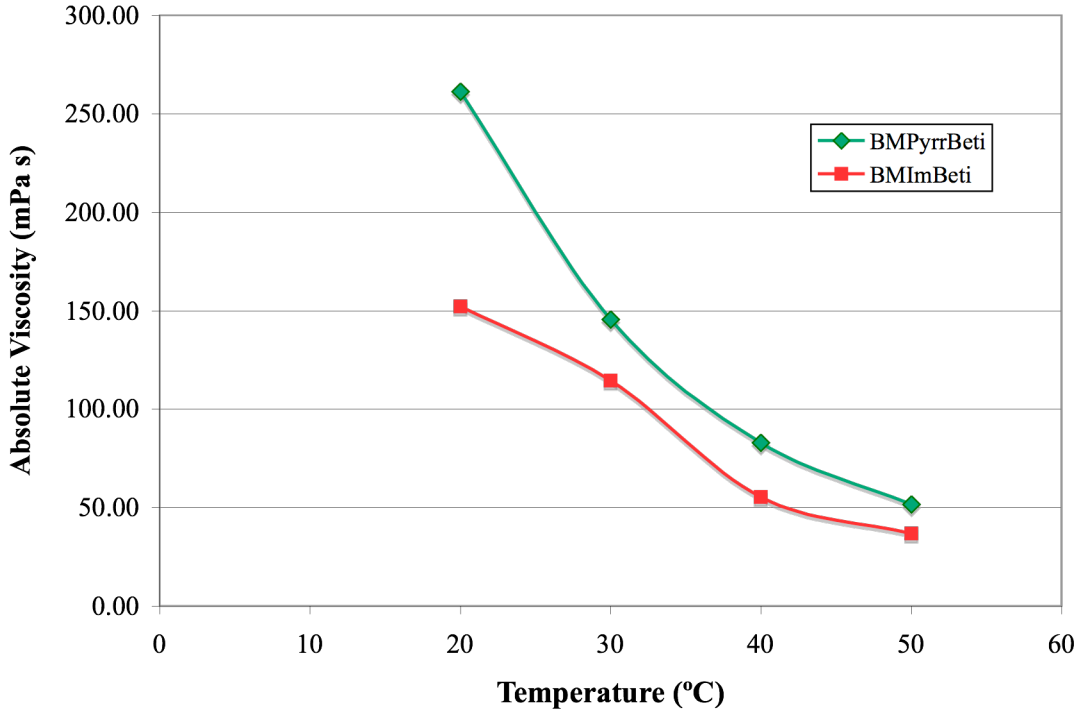

Figure 26. Absolute Viscosities (η) of 1-butyl-1-methyl-pyrrolidinium BETI and 1-butyl-3-methyl-imidazolium.

The absolute viscosities of several imidazolium-containing ionic liquids and several pyrrolidinium-containing ionic liquids are given in Table 16 and 17 below.

Table 15. The viscosities of some common imidazole-based and pyrrolidinium-based ionic liquids at 25 ºC.[22,2]

Temperatures are noted in parenthesis if other than 25 ºC.

Ionic liquid	Viscosity (mPa s)
$EMIBF_4$	32,37
$BMIBF_4$	75
$BMIPF_6$	182
$MMINTf_2$	44, 31
$EMINTf_2$	34(20), 28, 27
$PMINTf_2$	60
$BMINTf_2$	40 52(20), 56
$HMINTf_2$	71
EMIBeti	61(26)
BMIBeti	87

Ionic liquids	Viscosity η (mPa s)
	(+/- 0.1%)
$[Pyrr][NO_3]$	5.2
$[Pyrr][[HSO_4]$	190.1
[Pyrr][HCOO]	2.5
$[Pyrr][CH_3COO]$	30.2
$[Pyrr][CF_3COO]$	21
$[Pyrr][C_7H_{15}COO]$	36.5

Table 16. Viscosities of Densities of BMPyrrBeti at various temperatures.[2]

Temp (ºC)	Ave Time s	Viscometer constant mm^2/s^2	Kinematic viscosity mm^2/s (υ)	Kinematic viscosity cm^2/s (υ) Stoke	Density ρ g/mL (g/cm^3) *rho*	Absolute viscosity g/cm s Poise (η)	Absolute viscosity mPa s centiPoise (cη)
20	588.14	0.409	240.54926	2.4054926	1.085916667	2.612164506	261.2164506
30	322.87	0.4173	134.733651	1.34733651	1.08105	1.456538134	145.6538134
40	190.92	0.4035	77.03622	0.7703622	1.07585	0.828794173	82.87941729
50	119.85	0.4049	48.527265	0.48527265	1.064783333	0.51671023	51.67102298

Conductivity

The conductivity of 1-butyl-1-methyl-pyrrolidinium BETI was measured by in a temperature range between 21 and 153 ºC. The conductivity increased with increasing temperatures non-linearly. The conductance values of 1-butyl-1-methyl-pyrrolidinium

BETI and 1-butyl-3-methyl-imidazolium and are given in Table 18 and in Figure 27 below.

Table 17. Conductivity values for 1-butyl-1-methyl-pyrrolidinium Beti and 3-butyl-1-methyl-imidazolium-Beti.

BMPyrrBeti		BMImBeti	
Temperature (ºC)	Specific Conductivity κ (mS/cm)	Temperature (ºC)	Specific Conductivity κ (mS/cm)
21.6	0.61	22.7	1.53
31.2	1.04	33.9	3.45
46.1	2.21	41.5	4.54
54.4	2.95	51.5	6.24
63.3	3.86	52.5	6.95
74.1	5.58	63	8.63
89.2	8.02	76.9	12.13
99.7	9.89	78.4	13.54
105.5	11.45	95.5	19.05
118.7	14.58	102	23.39
122.4	15.28	103.7	23.28
125.5	16.27	113.9	27.87
128.8	17.02	123.1	31.63
142.4	20.79	133.1	35.81
153.1	25.31	146	41.03

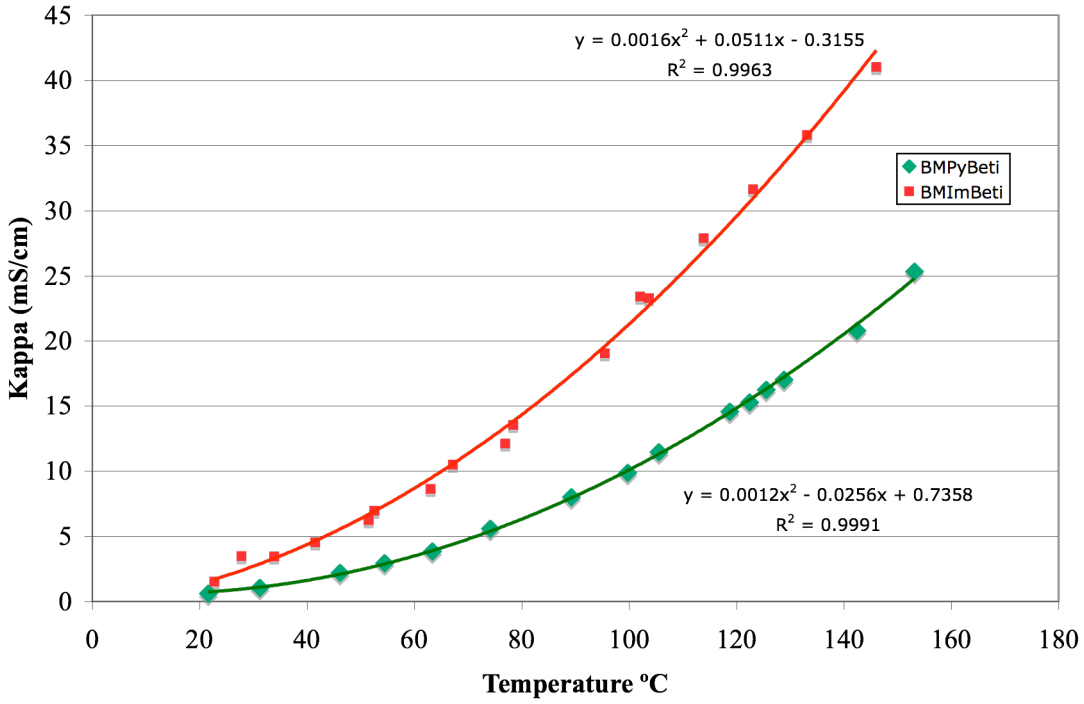

Figure 27. A plot of conductivity values for 1-butyl-1-methyl-pyrrolidinium Beti and 3-butyl-1-methyl-imidazolium-Beti as a function of temperature.

1-butyl-1-methyl-pyrrolidinium Beti is less conductive than 1-butyl-3-methyl-imidazolium. Conductivity is inversely proportional to viscosity (in general). This is because as a liquid's viscosity increases, its charge mobility decreases. 1-butyl-1-methyl-pyrrolidinium Beti was shown to be more viscous at all temperatures than 3-butyl-1-methyl-imidazolium-Beti, and therefore would be expected to exhibit lower conductivity.

The difference in conductivity increases as the temperature increases, though not linearly. At room temperature, the conductivities of the two ionic liquids do not show a significant difference in conductivity.

Thermal Properties

Comparison of the Thermal Properties of BMPyrrBeti and BMImBeti

The TGA curves of BMPyrrBeti and BMImBeti are shown in Figures 28 and 29. Both samples were subjected to the same thermal conditions, including type of instrument used, temperature range, temperature ramp rate, and baseline. Once the data were plotted, two points were measured; T_{start} (the temperature at which thermal decomposition begins to occur) and the T_{onset} (the temperature that falls at the intersection of lines drawn tangent to the % baseline weight, and the thermal decomposition curves).

Five runs were performed on BMPyrrBeti, and the average and standard deviations were obtained. Statistical analysis reveals that BMPyrrBeti has a T_{start} that is 18 ºC higher than that reported for BMImBeti, and a T_{onset} that is 22 ºC higher than that reported for BMImBeti, as shown in Table 19.

Table 18. Comparison of thermal properties of BMPyrrBeti and BMImBeti.

Ionic Liquid	T_{start} (°C)	T_{onset} (°C)
BMIBeti	314	410
BMPyBeti	332	432

BMPyrrBeti and BMImBeti differ only by their cation. The have the same alkyl substituents, a butyl- and a methyl- group (although both are attached to the same site on the pyrrolidine molecule), and the same anion. In the following table, the thermal properties of BMPyrrBeti were arbitrarily set at 100% so that the thermal properties of the other ionic liquid could be compared on a relative scale.

Table 19. T_{start} and T_{onset} values for 1-butyl-1-methyl-pyrrolidinium BETI and 3-butyl-1-methyl-imidazolium-BETI including the percent of T_{start} and T_{onset} as a function of BMPyrrBeti.

Ionic Liquid	T_{start} (˚C)	T_{onset} (˚C)	% of T_{start}	% of T_{onset}
BMPyBeti	**332**	**432**	**100**	**100**
BMIBeti	314	410	95	95

This table shows that between these two ionic liquids, differing the cation to Pyrrolidine affords the highest T_{start} and T_{onset} values, meaning that this ionic liquid is slightly more thermally-stable.

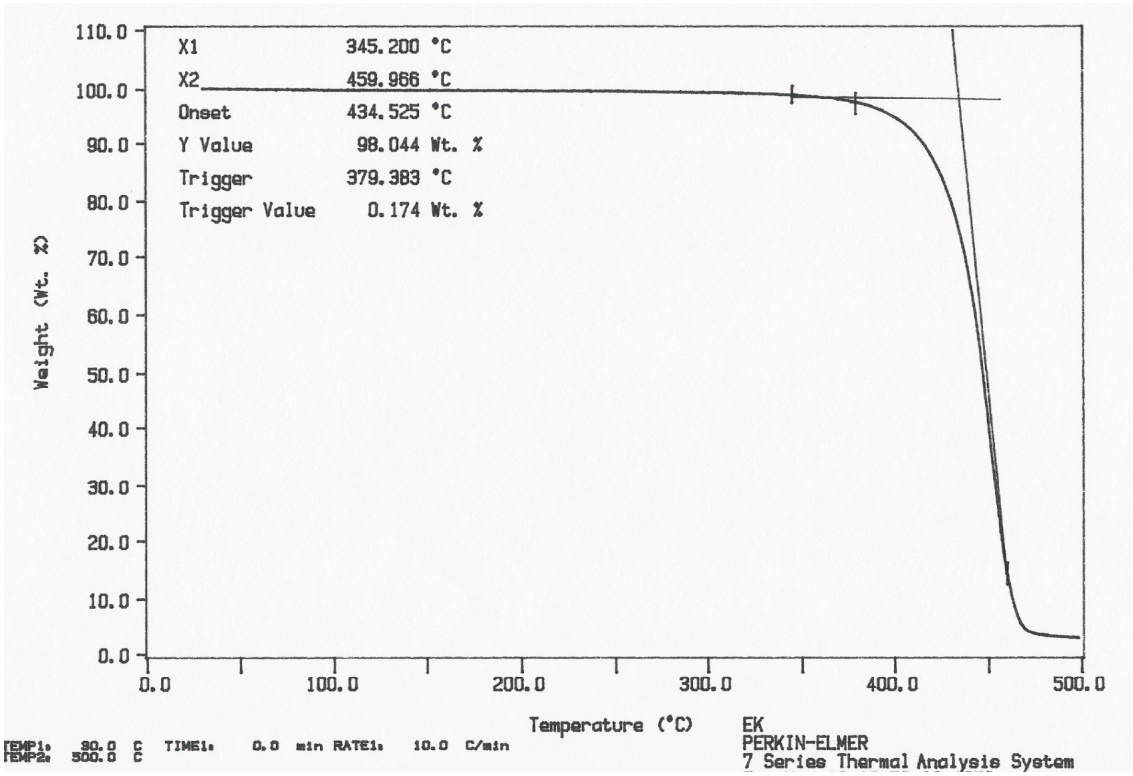

Figure 28. A TGA curve of BMPyrrBeti showing a T_{onset} of 434.525 °C

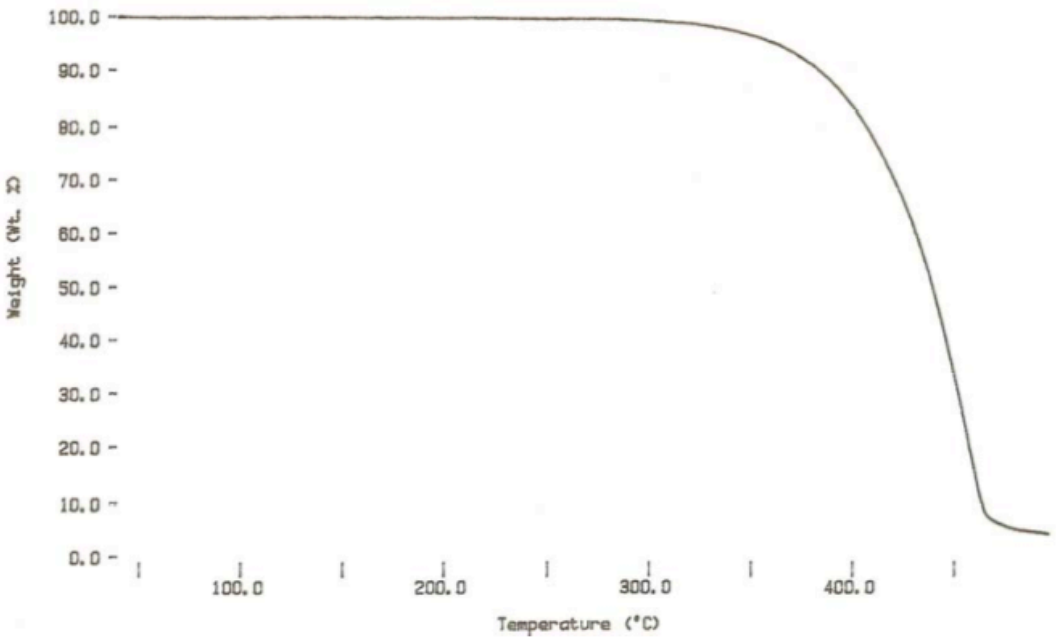

Figure 29. A TGA curve of BMImBeti showing a T_{onset} of 410°C

Table 20.Thermal decomposition temperatures of several imidazolium-based ionic liquids.

Ionic Liquid	**T_d(°C)**
$MMINTf_2$	444
$EMIPF_6$	375
$EMINTf_2$	439, 455
$PMIPF_6$	335
$PMINTf_2$	452
$BMIBF_4$	361, 425
$BMIPF_6$	433
$BMINTf_2$	427, 422
BMIBeti	402
$HMINTf_2$	428
C_8MINTf	425

Table 21. Glass transition temperatures t_g, melting points t_m, and decomposition temperatures t_d for selected prrolidinium and piperidinium ionic liquids.

	t_g	t_m	t_d
$[MPPyrro]^+[Tf_2N]^-$	-	7	343
$[MBPyrro]^+[Tf_2N]^-$	-86	-18	340
$[MOPyrro]^+[Tf_2N]^-$	-81	-	325
$[MBPyrro]^+[BF_4]^-$	-	78	310
$[MBPyrro]^+[AsF_6]^-$	-	66	325
$[MPPip]^+[Tf_2N]^-$	-	9	341
$[MBPip]^+[Tf_2N]^-$	-73	-	320
$[MOPip]^+[Tf_2N]^-$	-76	-	315
$[MOPip]^+[BF_4]^-$	-	92	325
$[MOPip]^+[N(CN)_2]^-$	-70	-	200
$[MOPip]^+[TfO]^-$	-	47	300

Differential Scanning Calorimetry

The DSC curve for BMPyrrBeti is shown in Figure 30. Upon cooling the DSC curve shows a positive sharp peak at -35º C which corresponds to a liquid-solid phase transition. Upon reheating the sample, a positive peak at -20º C is observed, which corresponds to a second phase transition. Upon further heating, a negative peak at ~ 8º C is observed, which is due to the melting of the ionic liquid.

The thermal behavior of six Pyrrolidine-based ionic liquids studied by Me´rie`m Anouti et al,[2] by means of DSC are reported in below. The data consist of the melting point (T_m), freezing point (T_{fr}), glass transition point (T_g), and decomposition temperatures (Td) of the six ionic liquids studied.

Table 22. Phase transition temperatures for several pyrrolidinium-based ionic liquids as measured by DSC.

	Temperature (ºC)		
	T_m	T_{fr}	T_g
[Pyrr][NO_3]	-15	-27	n.o.
[Pyrr][HSO_4]	-30	-45	-102
[Pyrr][HCOO]	-10	-60	-85
[Pyrr][CH_3COO]	-5	-65	-104
[Pyrr][CF_3COO]	-10	-48	n.o.
[Pyrr][$C_7H_{15}COO$]	-40	-53	-105

Determination of phase change with Differential Scanning Calorimetry

A sample weight of 15.635 g of 1-butyl-1-methyl-pyrrolidinium BETI was placed in a hermetically-sealed pan, and weighed on a Perkin-Elmer Micro-balance (model # 302-0051).

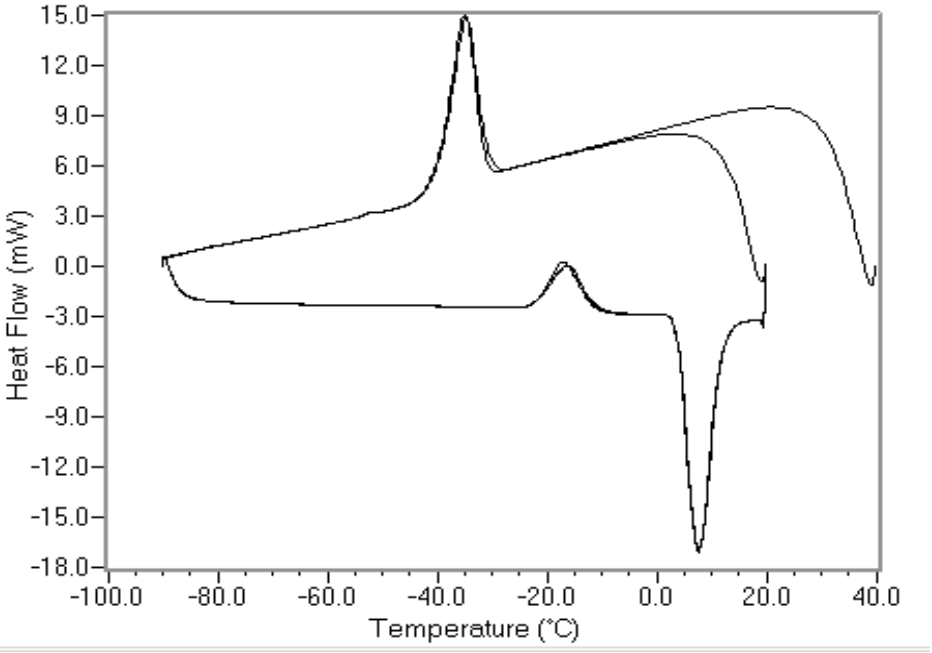

Figure 30. DSC of 1-butyl-1-methyl-pyrrolidinium Beti undergoing phase changes as a function of temperature.

On the initial negative sweep, the DSC curve shows a sharp positive peak at -37°C which corresponds to the melting of BMPyrrBeti. After reversing the temperature at -90ºC the DSC curve displays a positive peak at -21ºC and a negative peak at 8ºC. The peak at -21ºC is due to another phase change and the peak at 8ºC corresponds to the melting of the new phase of BMPyrrBeti.

Electrochemical Properties of BMPyrrBeti

The electrochemical window of BMPyrrBeti ionic liquid was determined by cyclic voltammetry using a glassy carbon electrode. The cyclic voltammogram obtained at 25ºC at 50 mV/s scan rate is shown in Figure 24. Like other ionic liquids containing the pyrrolidinium cation, the electrochemical window is much larger than was found in imidazolium-type ionic liquids. From figure 24, the electrochemical window is estimated to be ~ 6.5 V (-3.5 – 3.0 V). For comparison, the corresponding imidazolium ionic liquid BMImBeti shows an electrochemical window of ~ 4.5 V (Table 11, Figure 24).

Table 23. Electrochemical potential windows 1-butyl-1-methyl-pyrrolidinium BETI and 3-butyl-1-methyl-imidazolium-BETI.

Ionic Liquid	Positive Potential (V)	Negative potential (V)	Total Potential (V)
BMIBeti	**2.1**	**(-)2.4**	**4.5**
BMPyBeti	**3**	**(-)3.5**	**6.5**

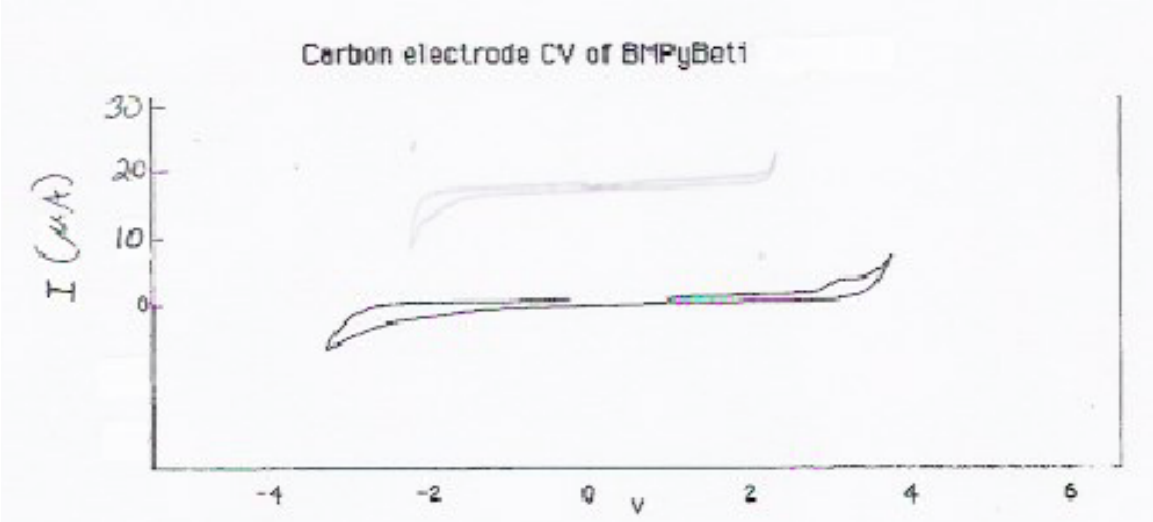

Figure 31. Cyclic voltammograms of BMImBeti at 80.6 ppm H_2O (top) and BMPyrrBeti at 106 ppm H_2O (below), using a glassy-carbon electrode at a 50mv/s scan rate.

Determination of the diffusion coefficient of BMPyrrBeti was done by CV data of ferrocene in BMPyrrBeti. First, the surface area of the GC (glassy-carbon) electrode was determined from CV data of 4 x 10^{-3} M ferrocene $Fe(C_5H_5)_2$ in acetonitrile (CH_3CN | 0.1 M NBu_4PF_6). For this solution, the diffusion coefficient was known to be $2.4x10^{-5}$ cm^2s^{-1}[26].

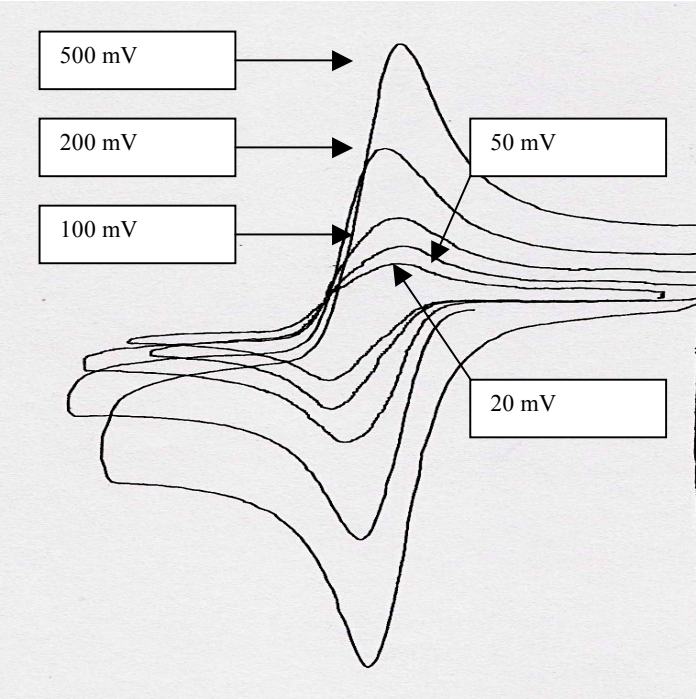

Figure 32. Cyclic Voltammograms of BMPyrrBeti to determine the surface area of the electrode.

Table 24. Data for the determination of the surface area of the electrode.

Scan Rate (V)	$(V/s)^{1/2}$	$(V/s)^{1/2}$
0.02	0.141	8.125E-06
0.05	0.224	1.075E-05
0.1	0.316	1.455E-05
0.2	0.447	2.298E-05
0.5	0.707	3.275E-05

The square root of the scan rate in V/s was plotted versus the current in amps (A) and the slope was determined.

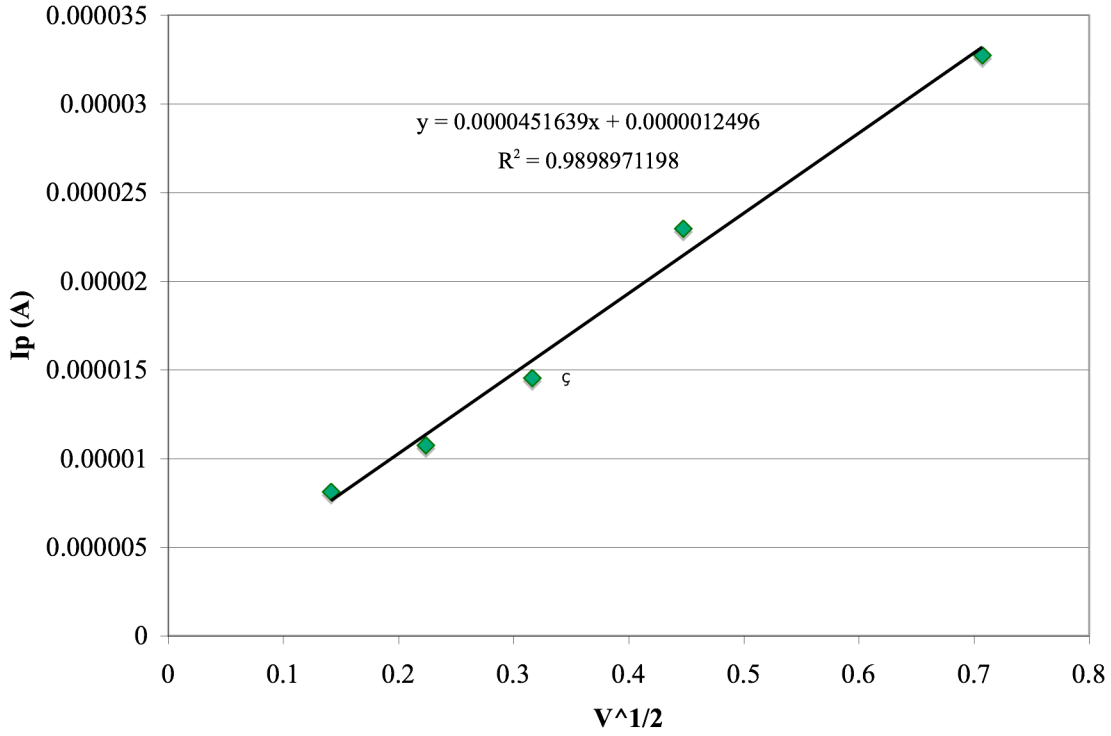

Figure 33. Determination of the surface area of the electrode.

From the Randles-Sevcik equation

$$I_p = 269 \cdot n^{3/2} \cdot D^{1/2} \cdot C_M \cdot A \cdot V^{1/2}$$

the surface area of the electrode was determined. A plot of $I_{p,a}$ vs $V^{1/2}$ gives a straight line (Figure 34, Table 24). From the slope of the line, the electrode surface area was calculated to be 0.857 mm^2.

$$A = \frac{slope}{269 \bullet n^{3/2} \bullet D^{1/2} \bullet C}$$

$$A = \frac{4.5164 \times 10^{-5}}{269 \bullet 1^{3/2} \bullet \left[\left(2.4 \times 10^{-5}\right)^{1/2} \text{cm}^2\text{s}^{-1}\right] \bullet 4 \times 10^{-3}\,\text{M}} = 0.00857\,\text{cm}^2 = 0.857\,\text{mm}^2$$

The surface area was determined to be 8.57 x 10^{-3} cm^2, or 0.857 mm^2.

The diffusion coefficient of BMPyrrBeti ionic liquid was determined from cyclic voltammograms of ferrocene in BMPyrrBeti. Cyclic voltammograms of ferrocene in BMPyrrBeti at different scan rates are shown in Figure 35. The anodic peak current at different scan rates are given from the Randles Sevcik equation.

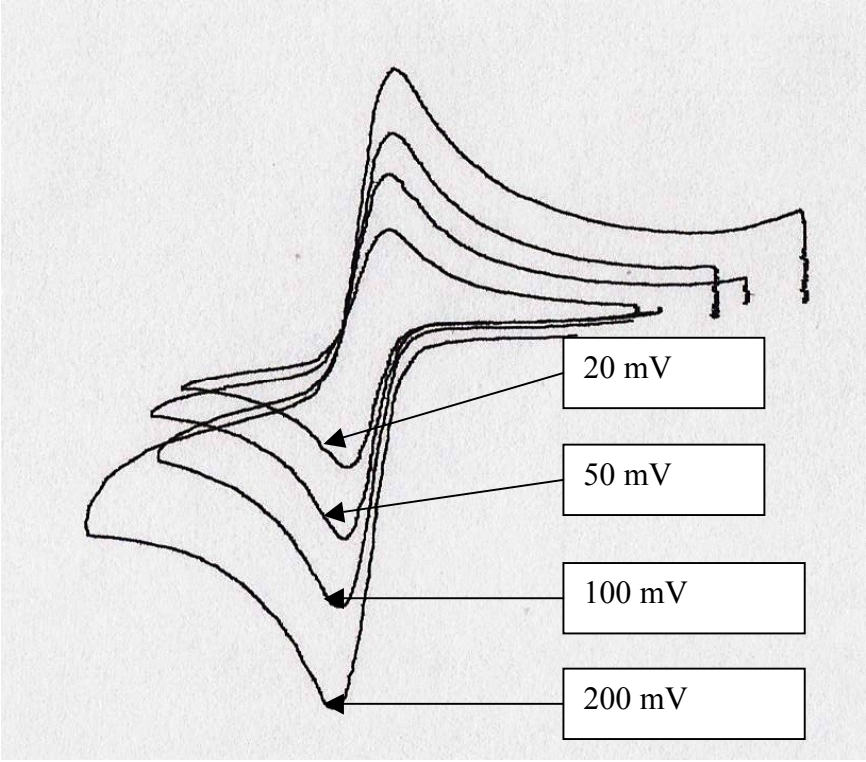

Figure 34. Cyclic Voltammograms of ferrocene at 25.4 °C in acetonitrile at varying scan rates.

Table 25. Data for the determination of the diffusion coefficient of BMPyrrBeti at 25.4 °C in 6.045 x 10^{-5} M ferrocene, with NBu_4PF_6 as supporting electrolyte.

Scan Rate (V)	(V/s)1/2	Ip,a (A)
0.02	0.141	5.750E-06
0.05	0.224	8.375E-06
0.1	0.316	1.020E-05
0.2	0.447	1.438E-05
0.5	0.707	1.898E-05

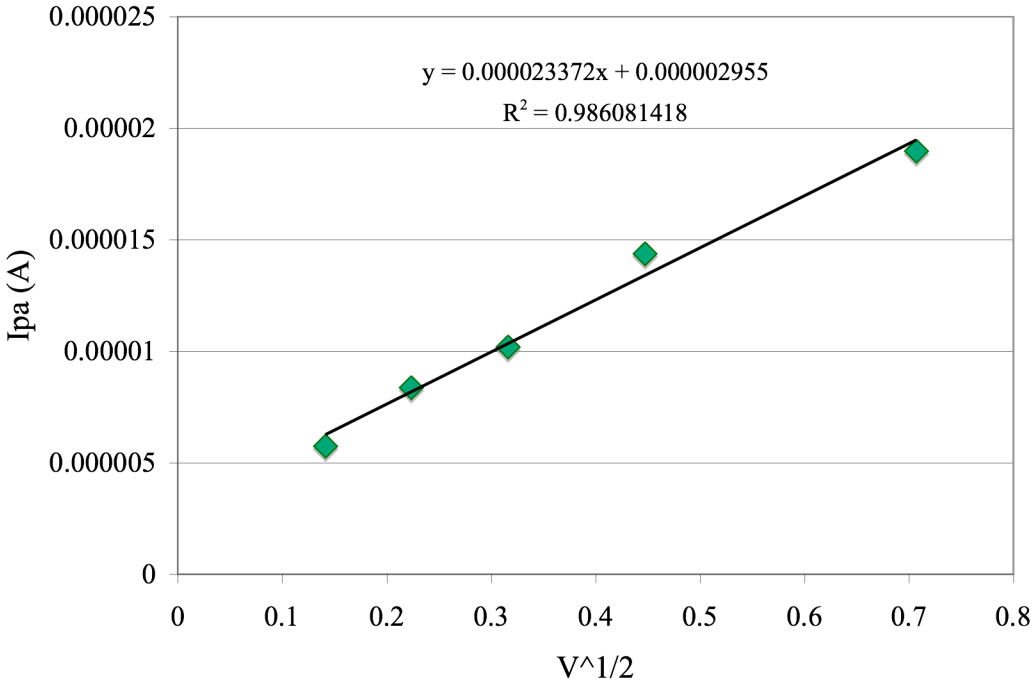

Figure 35. Peak current values versus the square root of the scan rate.

$$I_p = 269 \cdot n^{3/2} \cdot D^{1/2} \cdot C_M \cdot A \cdot V^{1/2}$$

$$\frac{Ip}{V^{1/2}} = slope = 269 \quad n\,3/2 \quad D1/2 \quad CM \quad A \quad V^{1/2}$$

$$I_p = K \cdot V^{1/2}$$

$$K = slope = 269 \cdot n^{3/2} \cdot D^{1/2} \cdot C_M$$

A plot of I_p vs. $V^{1/2}$ gives a straight line from which a diffusion coefficient for BMPyrrBeti was observed to be 2.81 x 10^{-8} cm^2/s at 24.5 ºC.

$$D^{1/2} = \frac{2.33724 \times 10^{-5}}{269 \bullet 1^{3/2} \bullet 0.00857\ cm^2 \bullet 0.060456 M} = D^{1/2} = 1.68 \times 10^{-4} \qquad D = 2.81 \times 10^{-8}$$

The diffusion coefficient of BMPyrrBeti at 50 ºC was obtained in an analogous way. The CV and anodic peak current at different scan rates are shown in figure 37 and Table 26. From this slope the diffusion coefficient of BMPyrrBeti at 50 ºC was determined to be 5.21 x 10^{-7} cm^2/s.

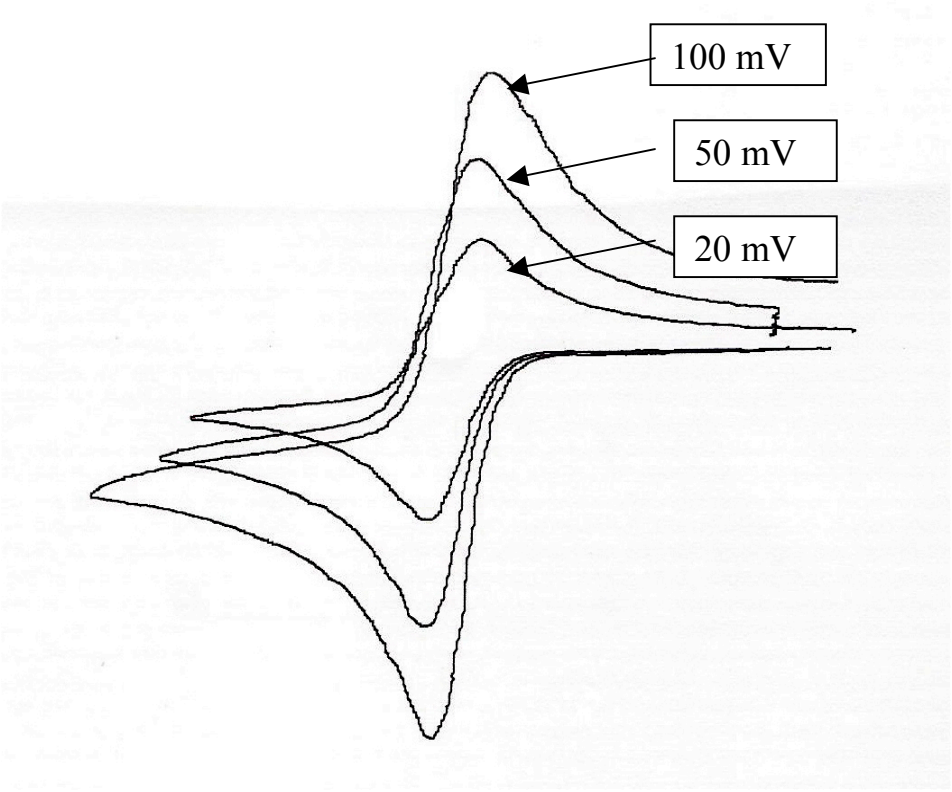

Figure 36. Cyclic Voltammograms of ferrocene at 50 °C in acetonitrile at varying scan rates.

Table 26. Data for the determination of the diffusion coefficient of BMPyrrBeti at 50 °C in 6.045 x 10^{-5} ferrocene, with NBu_4PF_6 as supporting electrolyte.

Scan Rate (V)	(V/s)1/2	Ip,a (A)
0.02	0.141	1.375E-05
0.05	0.224	2.000E-05
0.1	0.316	3.125E-05

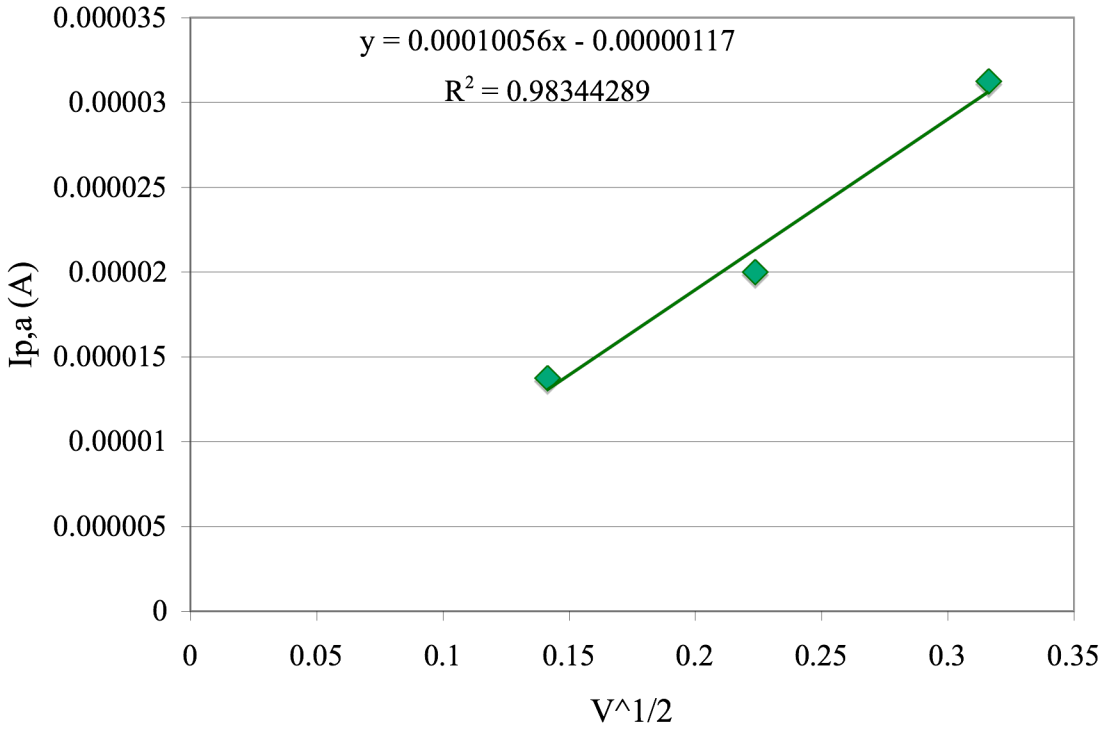

Figure 37. A plot of $I_{p,a}$ vs $V^{1/2}$ obtained for ferrocene in BMPyrrBeti at 50 ºC.

Using this slope in the Randles-Sevcik equation, the diffusion coefficient was determined:

$$D^{1/2} = \frac{1.01 \times 10^{-4}}{269 \bullet 1^{3/2} \bullet 0.00857\ cm^2 \bullet 0.060456 M} = D^{1/2} = 7.22 \times 10^{-4} \qquad D = 5.21 \times 10^{-7}$$

Thus, the diffusion coefficient for 6.05 x 10^{-2} M ferrocene in BMPyrrBeti at 50 ºC is 5.21 x 10^{-7} cm^2/s.

CONCLUSION

A comparison of the physical and electrochemical properties of BMPyrrBeti and BMImBeti ionic liquids showed that BMPyrrBeti had a much wider potential window (6.4 V) than the corresponding ionic liquid (BMImBeti) containing the imidazolium cation (~4.2 V).

The density of the new ionic liquid fell within the expected range for ionic liquids, being only slightly more dense than water. The density decreased as the temperature increased. At the temperature range measured (20 ºC – 50 ºC), the newly-synthesized pyrrolidine-based ionic liquid, was between 72.6% - 71.9% as dense as the imidazole-based ionic liquid.

The kinematic and absolute viscosities of the new pyrrolidine-based ionic liquid were higher than that of the imidazole-based ionic liquid, although this feature diminished as temperature increased. Viscosity is generally inversely-correlated to the conductivity of the ionic liquid, and that was seen experimentally with the pyrrolidine-based ionic liquid.

At 20 ºC, the conductivity of 1-butyl-1-methyl-pyrrolidinium Beti is nearly identical to 3-butyl-1-methyl-imidazolium-Beti. However, as temperature rises, the difference in conductivity becomes greater. This was unexpected form a purely viscosity-based standpoint. Because the difference in viscosity diminished as the temperature rose, the conductivity difference should also diminish. The reverse of this was observed instead, again demonstrating that relative viscosity alone does not always predict relative

conductivity. Other factors that contribute to transport properties are ion dissociation, as well as ion shape and radius.[15]

The diffusion coefficient of BMPyrrBeti as determined from the CV of Ferrocene was $D = 2.81 \times 10^{-8}$ cm^2/s at 24.5 ºC, and $D = 1.39 \times 10^{-7}$ cm^2/s at 50 ºC.

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APPENDIX

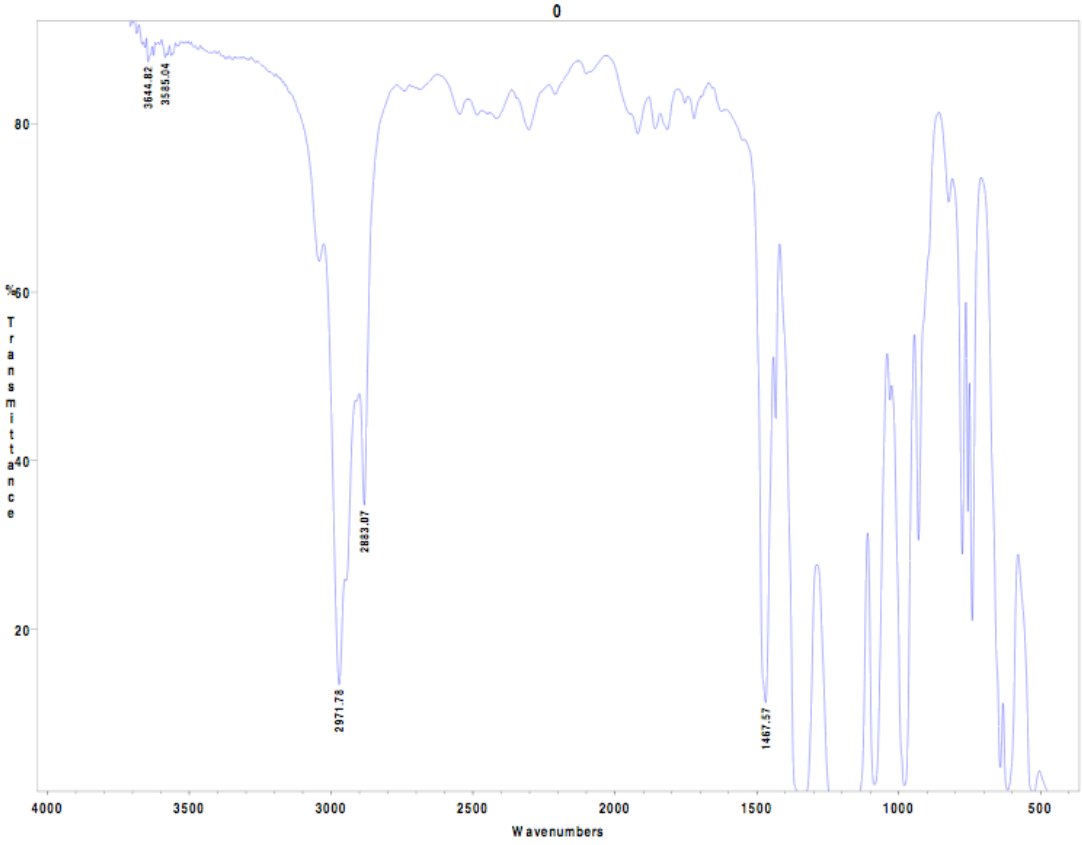

Figure 38. IR Spectra of $BMPyrr^{+}Beti^{-}$ containing 91 ppm

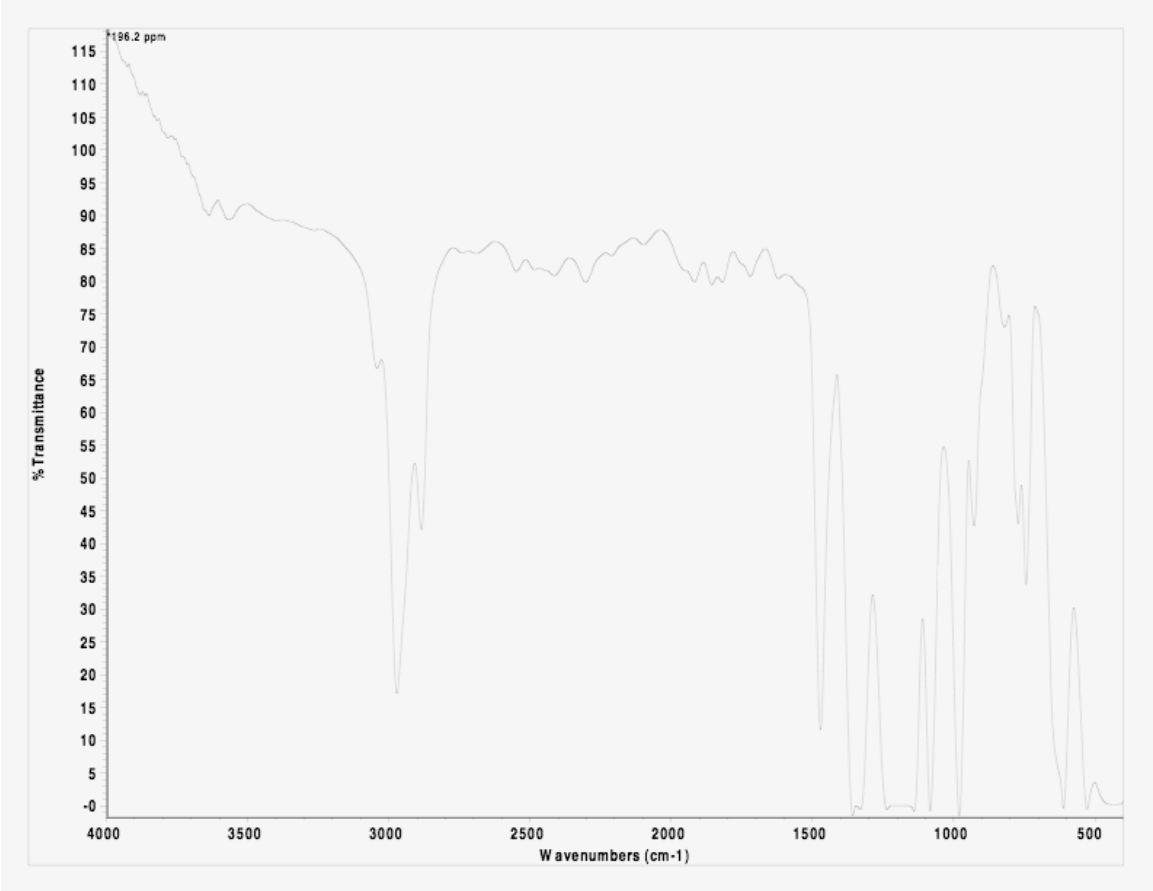

Figure 39. IR Spectra of $BMPyrr^{+}Beti^{-}$ containing 196 ppm

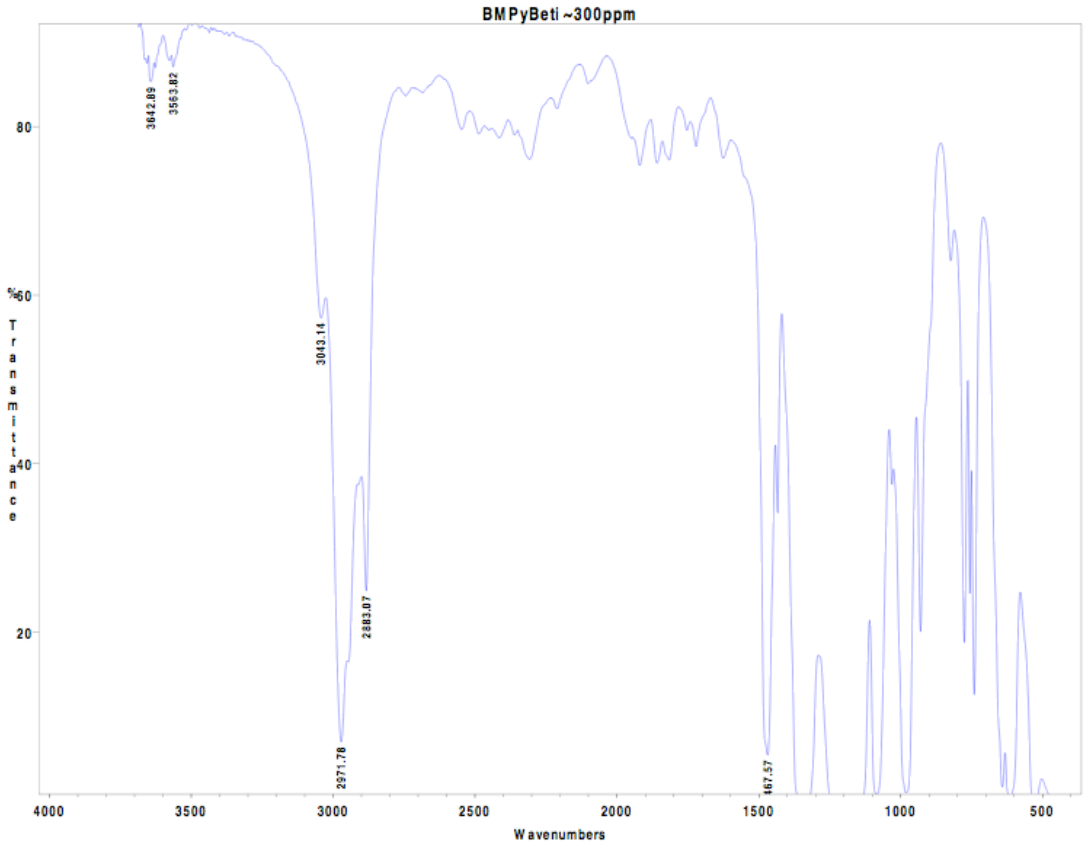

Figure 40. IR Spectra of $BMPyrr^{+}Beti^{-}$ containing 300 ppm

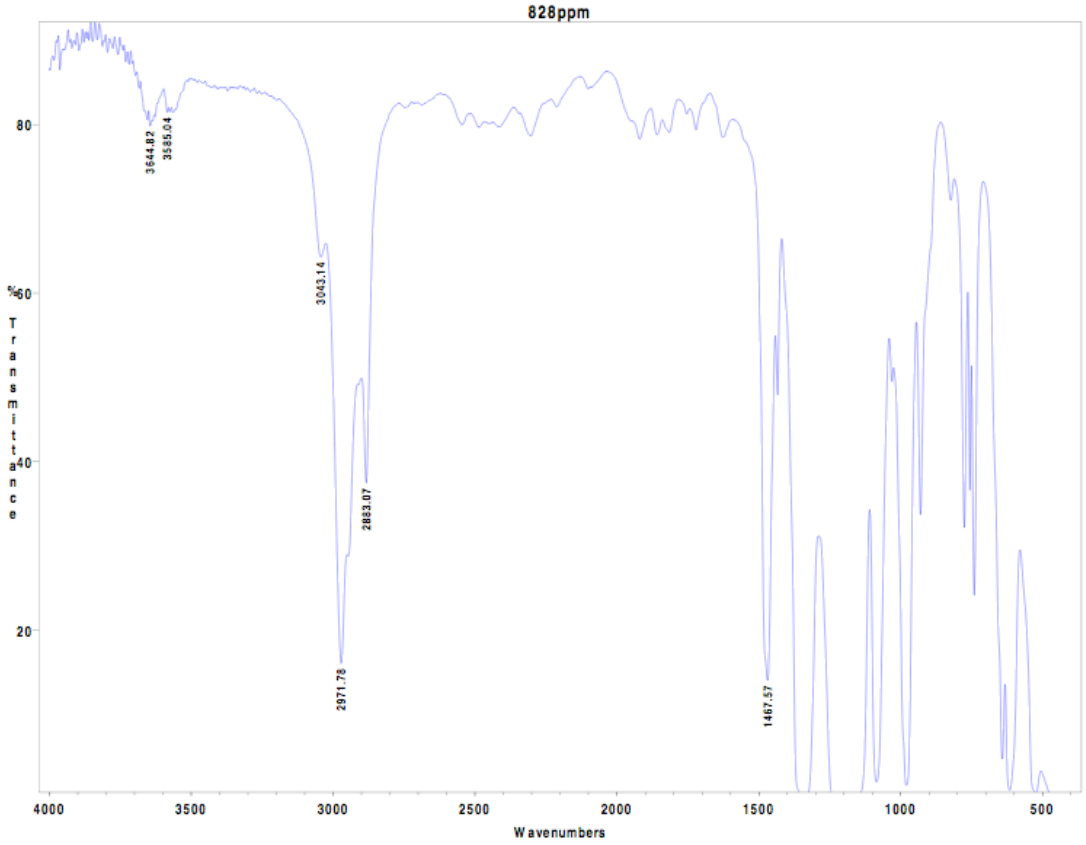

Figure 41. IR Spectra of $BMPyrr^{+}Beti^{-}$ containing 828 ppm

Figure 42. IR Spectra of $BMPyrr^{+}Beti^{-}$ containing 1647 ppm

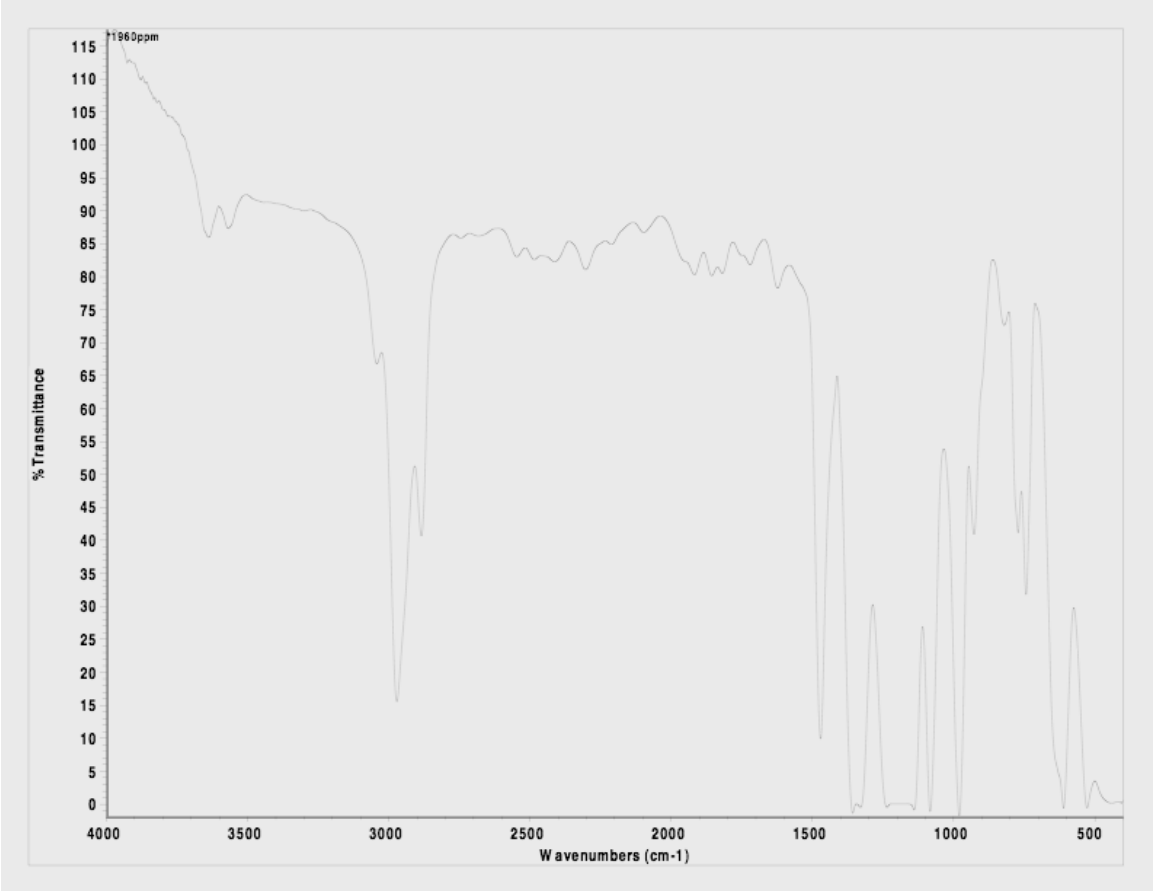

Figure 43. IR Spectra of $BMPyrr^{+}Beti^{-}$ containing 1960 ppm

Fourier-Transform Nuclear Magnetic Resonance

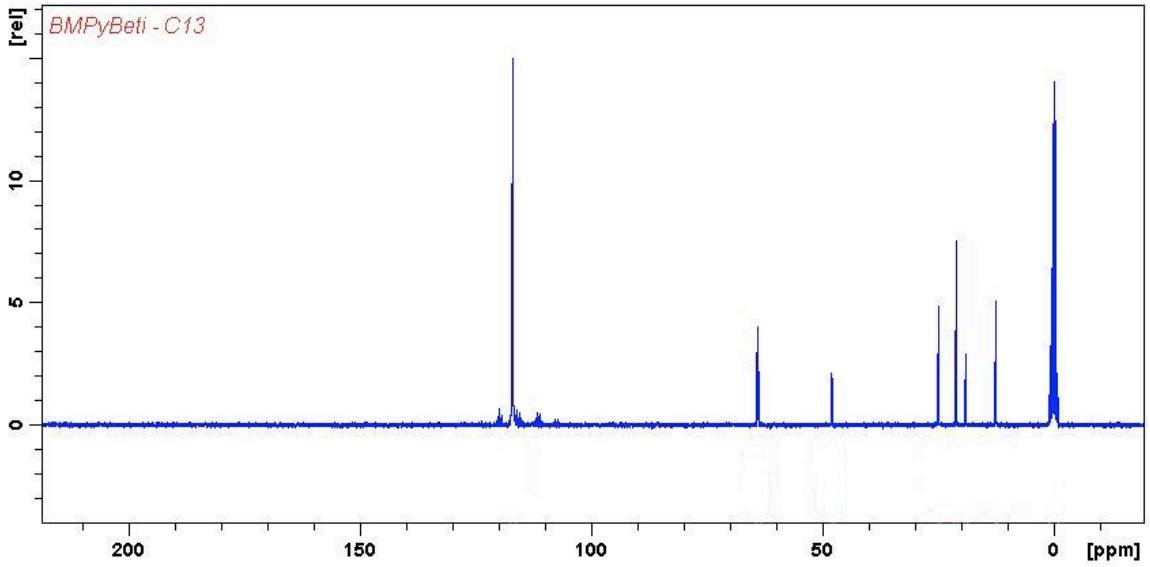

Figure 44. Carbon-13 NMR of $BMPyrr^{+}Beti^{-}$

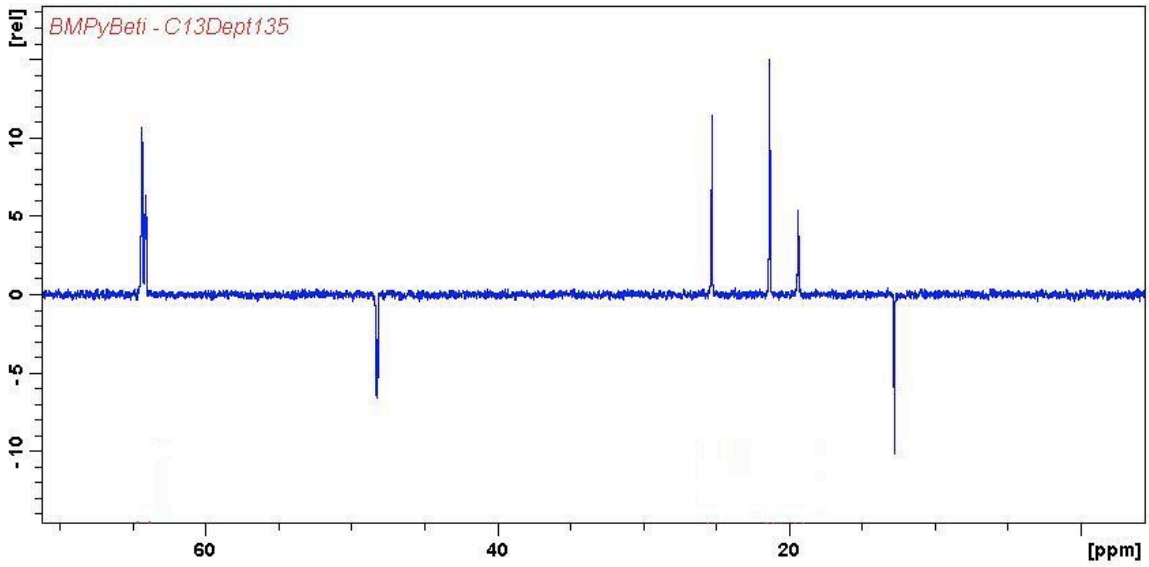

Figure 45. DEPT-135 NMR of $BMPyrr^{+}Beti^{-}$

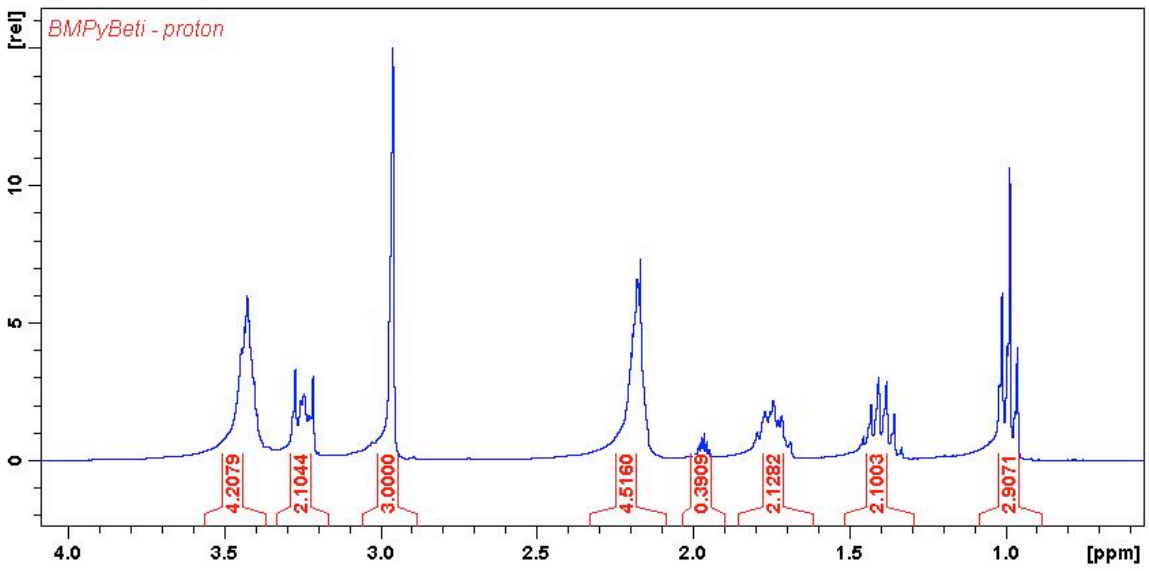

Figure 46. Proton (H^+) NMR of $BMPyrr^+Beti^-$